DISSOLUTION OF IRON OXIDE

IN

AQUEOUS SOLUTIONS OF SULPHUR DIOXIDE

by

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B.Sc., University of Birmingham, 1964

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in the Department

of

METALLURGY

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

July, 1966

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Date __July 27, 1966_____

ABSTRACT

A study has been made of the dissolution of naturally occurring α-iron oxide hydrate in acidified aqueous solutions of sulphur dioxide at 110°C. The dissolution was found to be independent of acidity at low concentrations of sulphur dioxide and inversely dependent on acidity at higher concentrations of sulphur dioxide. Both homogeneous and heterogeneous control of the reaction was observed. The addition of cupric ion to the system catalysed the rate. Dissolution is thought to occur via hydration of the oxide surface and subsequent reaction of undissociated sulphurous acid at the surface to form a ferric-sulphite complex. The rate determining step is considered to be the desorption of the complex from the surface.

A limited study of the direct dissolution of iron oxide hydrate in sulphuric and perchloric acids at temperatures between 120 and 150°C is included. Under these conditions, the hydrated oxide surface is thought to undergo anion exchange during dissolution.

Work carried out on the preparation and identification of the isomeric α- and γ-iron oxide hydrates is reported.

ACKNOWLEDGEMENT

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INTRODUCTION

General

The problems associated with the removal of iron oxides from industrially important silicate materials have recently been reviewed[1]. Dithionites, or organic derivitives of dithionites, have traditionally been used for this purpose. Leaching with dithionites is carried out at room temperatures. These reducing agents are relatively expensive when compared with the price of sodium bisulphite. Preliminary experiments had indicated that leaching of iron oxides with bisulphite could be very rapid under typical pressure leaching conditions.

This study was undertaken to try to establish the rate determining steps in the reaction of bisulphite ion with iron oxides at elevated temperatures and pressures. It was decided to use specifically hydrated iron oxides (FeOOH) since the bulk of the leachable iron in clay minerals is present in this form.

It was also hoped that this study would contribute information which would assist in assessing the feasibility of the solution mining of hydrated iron oxide ores with aqueous solutions of sulphur dioxide[2].

Review of Literature

Most of the previous investigations into the reactions of ferric ion with sulphurous acid have been carried out on homogeneous systems at room temperatures, the only exception being very limited studies using freshly precipitated ferric hydroxide as the source of iron[3,9,10].

Although this investigation is concerned with the reactions of solid iron oxide hydrates with aqueous solutions of sulphur dioxide at elevated temperatures, the previous work on homogeneous systems is reviewed here since it is pertinent to the present problem.

A certain amount of work has been carried out on the reactions of solid manganese oxides with sulphurous acid. This work is also reviewed since it introduces concepts which may be applicable to the present work. The literature is discussed, as far as possible, in chronological order.

One of the earliest reports of reactions of the iron-sulphurous acid system was that of Berthier[4] who observed the formation of a red solution when sulphur dioxide was passed into a suspension of ferric hydroxide at room temperature. The red solution, which is now thought to be due to the formation of a ferric-sulphur IV complex, slowly becomes pale green on standing, and ferrous sulphate ($FeSO_4$) and ferrous dithionate (FeS_2O_6) are formed. (Gelis[5])

Heeren[3] studied the reactions between sulphurous acid and pyrolusite, MnO_2, and also manganite, $Mn_2O_3 \cdot H_2O$. He found that the products of the oxidation of sulphurous acid by these oxides were

sulphate and dithionate in various proportions. He attributed the varying

proportions of oxidation products to the following factors:

    i) Temperature - high temperatures caused high

        yields of sulphate by decomposition of dithionate.

   ii) Composition of the mineral - presence in the

        dioxide of $Mn_2O_3H_2O$ gave more sulphate than

        dithionate.

    Bassett and Henry[9] investigated the effects of a large number

of oxidising agents on sulphurous acid at room temperatures. For the

case of metal ions easily reducible to a lower valency state, or to the

metal, they found that the proportions of dithionate and sulphate produced

depended almost entirely on the nature of the metal involved and were

independent of the concentration of the reactants, and the acidity.

They concluded that their experimental results could be accounted for by

postulating the formation of a complex addition product from the metal

ion and sulphurous acid. The complex ion then decomposes very rapidly

by self-oxidation and reduction, involving an electron transfer from the

non-metal group to the metal ion. The decomposition can take place in

two different and independent manners to yield either sulphate or

dithionate. They considered that the complex ion is a metal - sulphite

complex. The postulated mechanisms for the decompsition of this complex

metal-sulphite ion are summarised in the following sequence of reactions:

Oxidation by ferric ion is used as an example. The structure of the

complex ion is not known but is represented here in its simplest form:

$$\text{i) } Fe^{+++} + SO_3^{=} \longrightarrow Fe^{+++}(SO_3^{=}) \qquad \text{Complex Ion Formation}$$

$$\text{ii) } Fe^{+++}(SO_3^{=}) \xrightarrow[\text{transfer}]{\text{electron}} Fe^{++}(SO_3^{-}) \qquad \text{Self Oxidation and Reduction}$$

$$\text{iii) } 2Fe^{++}(SO_3^{-}) \longrightarrow 2Fe^{++} + S_2O_6^{=} \qquad \text{Dithionate Formation}$$

$$\text{iv) } 2Fe^{++}(SO_3^{-}) \longrightarrow 2Fe^{++} + SO_3^{=} + SO_3$$

$$\text{v) } SO_3 + H_2O \xrightarrow{\text{rapid}} SO_4^{=} + 2H^{+} \qquad \left.\begin{array}{l} \\ \end{array}\right] \text{Sulphate Formation}$$
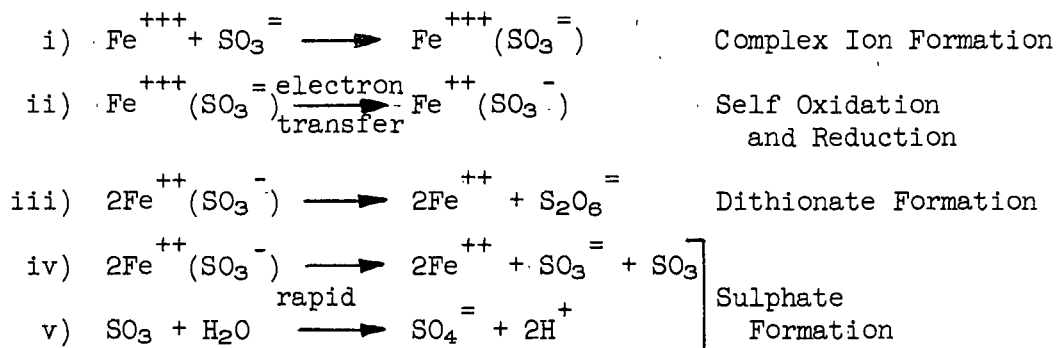
The authors consider that this mechanism is in agreement with their experimental observations, since the same complex gives rise to either sulphate or dithonate by reactions of the same order. Because the reactions are of the same order, they state that proportions of the two oxidation products should be essentially independent of concentration and acidity, and depend almost entirely on the nature of the oxidising metal ion. The nature of the metal ion would presumably govern the relative probabilities of the occurrence of reactions (iii) and (iv). Their supposition for the sulphite ion being the complex-forming anion, rather than the bisulphite ion, is partly based on the fact that a similar complex is thought to be formed in the reaction of cupric ions with sulphite ions under alkaline conditions[8].

The work of Bassett and Henry was extended by Bassett and Parker[10]. These authors studied the oxidation of sulphurous acid at room temperature by oxides of manganese, by ferric and cupric salts, and by molecular oxygen in the presence of various dissolved salts. They showed that oxidation by solid manganese oxides occured on the oxide surface. The proportions of dithionate and sulphate formed were specific for each polymorph, but were independent of all other factors examined. They concluded that dithionate can only be formed when the

oxide is reduced in one-electron steps. The mechanism they proposed is essentially similar to that proposed by Bassett and Henry, except that it involves the surface adsorption of sulphite ions, rather than complex ion formation in solution. The adsorbed sulphite ions are either discharged in two successive single-electron steps to yield sulphate, or two of them after partial discharge, unite to form a dithionate ion.

In the case of freshly prepared ferric hydroxide, they concluded, from visual observation of a red colouration, that the reaction involved the formation of a complex ferric-sulphite ion in solution, instead of a surface reaction. Thus the ferric hydroxide dissolved before it was reduced.

The reaction mechanisms proposed by Bassett and Henry and Bassett and Parker were part of the evidence that led Higginson and Marshall[11] to propound a general theory which applies to the oxidation of certain non-metallic compounds. The compounds in question are those which, when oxidised or reduced in homogeneous solution, give proportions of products which vary with the oxidising or reducing agent used. These authors took the reaction mechanism which has been proposed for the oxidation of hydrazine in aqueous acid, and showed that it also applied to the oxidation of sulphurous acid. They then used this mechanism as a basis for some generalizations concerning certain other oxidation-reduction reactions.

In this general scheme, two mechanisms operate, and oxidising agents were divided into three classes, depending on whether their reactions indicated one, the other, or both of these mechanisms. The

three classes of oxidising agents were called "1-equivalent, 2-equivalent, or 1,2-equivalent oxidising agents".

The two mechanisms that were proposed may be written as:

1) Reactions with 1-equivalent oxidising agents:-

i) $X^n \xrightarrow{\text{1-equiv.}} X^{n+1}$ Initial oxidation process

ii) $2X^{n+1} \longrightarrow (X^{n+1})_2$ Dimerisation of radicals

iii) $2X^{n+1} \longrightarrow X^{n+2} + X^n$ Disproportionation of radicals

iv) $X^{n+1} \longrightarrow X^{n+2}$ Further oxidation of radical
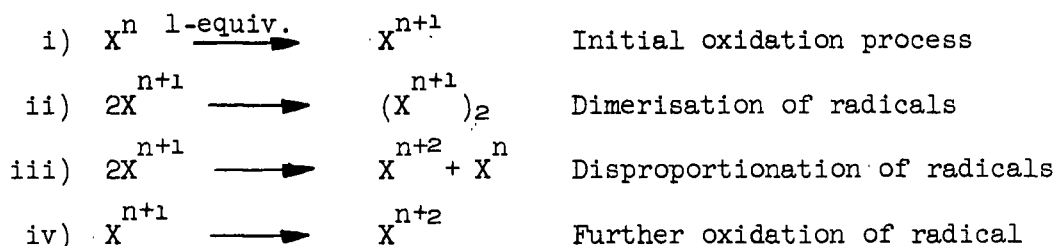
2) Reactions with 2-equivalent oxidising agent:-

v) $X^n \xrightarrow{\text{2-equiv.}} X^{n+2}$
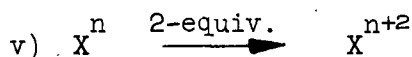
1,2-equivalent oxidising agents can react according to both of these mechanisms.

X^n represents a simple compound of a non-metallic element in oxidation state "n". The initial product of a 1-equivalent oxidation, X^{n+1}, is usually a free radical and can disappear by reactions (ii), (iii) or (iv).

Thus, from reactions (i) through (v), it may be seen that 2-equivalent reagents should oxidise X^n to X^{n+2} only, while 1-equivalent oxidising agents should produce $[X^{n+1}]_2$ and X^{n+2} in proportions varying with the reaction conditions.

In the case of sulphurous acid, X^{n+2} represents sulphate, $SO_4^=$, and $[X^{n+1}]_2$ represents dithionate, $S_2O_6^=$.

Higginson and Marshall found that, for oxidation-reduction reactions between transition metal ions or compounds and ions derived from non-transition elements, oxidation may occur in either 1- or 2-equivalent steps, the 1-equivalent step occuring more often. In the case of ferric iron, the oxidation state which would be formed after a 2-equivalent reaction, ie Fe^+, is unknown. Thus the reduction of ferric iron must take place by 1-equivalent reactions and so the oxidation products should include dithionate as well as sulphate.

In order to substantiate their theory on the mechanism of 1-equivalent reactions, Higginson and Marshall studied the reactions of ferric iron with sulphurous acid in the presence of cupric ion. They showed that the mechanism of this reaction agreed with the proposed 1-equivalent reagent mechanism. The suggested mechanism for this system involved the production of the thionate free radical (HSO_3), and consisted of the following sequence of reactions.

$$(i) \quad Fe^{3+} + HSO_3^- \xrightarrow{k_1} Fe^{2+} + HSO_3$$

$$-(i) \quad Fe^{2+} + HSO_3 \xrightarrow{k_{-1}} Fe^{3+} + HSO_3^-$$

$$(ii) \quad 2HSO_3 \xrightarrow{k_2} H_2S_2O_6$$

$$(iii) \quad Fe^{3+} + HSO_3 + H_2O \xrightarrow{k_3} Fe^{2+} + SO_4^= + 3H^+$$

$$(iv) \quad Cu^{2+} + HSO_3 + H_2O \xrightarrow{k_4} Cu^+ + SO_4^= + 3H^+$$

$$(v) \quad Cu^+ + Fe^{3+} \xrightarrow{rapid} Cu^{2+} + Fe^{2+}$$
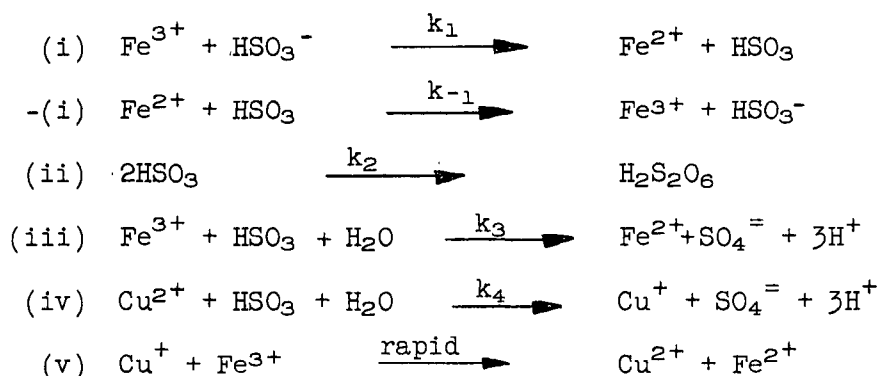
These authors state that, under their conditions, ie. $[H^+]$ = 0.08M at 25°C, there was no visual evidence for the formation of an iron (III)-sulphur (IV) complex, neither were they able to interpret their kinetic data on the basis of the formation of such a complex.

A mechanism involving, but not necessarily dependent upon, the formation of an iron (III)-sulphur (IV) complex was proposed by Karraker[13]. This mechanism postulates the formation and reactions of a ferric-bisulphite complex, and also the thionate free radical:

i) $H_2SO_3 \underset{}{\overset{K_1}{\rightleftharpoons}} H^+ + HSO_3^-$

ii) $Fe^{3+} + HSO_3^- \underset{}{\overset{K_2}{\rightleftharpoons}} Fe(HSO_3)^{2+}$

iii) $Fe(HSO_3)^{2+} \xrightarrow{k_1} Fe^{2+} + HSO_3$

iv) $HSO_3 + Fe^{2+} \xrightarrow{k_2} Fe^{3+} + HSO_3^-$

v) $HSO_3 + Fe^{3+} + H_2O \xrightarrow{k_3} SO_4^{2-} + Fe^{2+} + 3H^+$
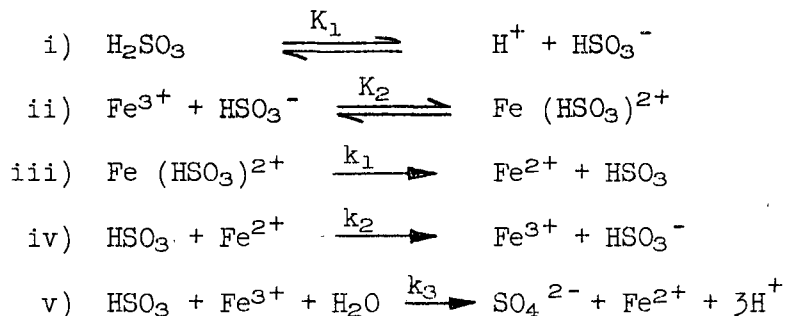
Karraker designed his reaction conditions to produce sulphate, rather than dithionate, by having a large excess of ferric iron and low concentrations of both reactants. Under these conditions, thionate radicals produced by reaction (iii) are likely to react with ferric ion to produce sulphate, as in reaction (v), rather than to react with another thionate radical and dimerise to form dithionate. The assumption of a ferric-bisulphite complex does not affect the rate expression for this mechanism, but it was included because of the obvious colour change that occurs on the addition of sulphurous acid to ferric ion. This was considered strong evidence for the formation of a complex.

The formation of a red colouration in solutions containing ferric ions and sulphurous acid under certain conditions is widely reported, and the colouration is generally attributed to complex ion formation.

The composition of this complex, or complexes, appears to be uncertain. Two types of complex are possible in the ferric iron-sulphurous

acid system: ferric-sulphite complexes and ferric-bisulphite complexes.

The structures of these two series of complexes may be represented as

$[Fe^{III}(SO_3)_n]^{3-2n}$ and $[Fe^{III}(HSO_3)_n]^{3-n}$ respectively. Depending on the

number of anions involved, the complexes could be anionic or cationic.

Bassett and Parker suggested that ferric-sulphite complexes with n=3 and

n=2 are possible. Danilczuk and Swinarski[12] carried out a photometric

study of the ferric-sulphite system. They showed that $[Fe^{III}(SO_3)_3]^{3-}$

is formed and is stable under conditions of excess $SO_3^=$. At low con-

centrations of sulphite ion ($Fe^{3+}:SO_3^= = 1:1$ or 1:2), it was suggested

that a self oxidation-reduction of the complex takes place leading to the

formation of complexes containing two and one sulphite ions, and also to

the formation of dithionate and ferrous ions. It was concluded that

equilibria exist between $[Fe^{III}(SO_3)_n]^{3-2n}$ and Fe^{++} and $\frac{n}{2}S_2O_6^=$.

To this author's knowledge, no direct evidence has been forth-

coming to show that complexes involving ferric and bisulphite ion occur.

The cationic complex $[Fe^{III}HSO_3]^{++}$ has been suggested[13].

The formation of the thionate free radical (HSO_3), or its

anion (SO_3^-), was first postulated by Franck and Haber[7] as occurring during

the oxidation of sulphurous acid by free oxygen. The existence of this

free radical seems to have been generally accepted, and it is thought to be

formed during the reactions of most oxidising agents with sulphurous acid.

Apart from reactions involving anionic species derived from

sulphurous acid, it has also been suggested that neutral sulphur dioxide

molecules can take part in the oxidation reactions. For the case of

oxidation by chromic and permanganic acids, Bassett and Parker[10] postulated that the complex metal ion was formed by the addition of neutral sulphur dioxide molecules rather than sulphite ions. The structure of such a complex ion was suggested to be:

$$\left[\begin{array}{c} O \\ O \end{array} \!\!\!\! \searrow \!\!\! Mn \!\!\! \nearrow\!\!\!\!\! \begin{array}{c} O \\ O \longrightarrow SO_2 \end{array} \right]^{-}$$
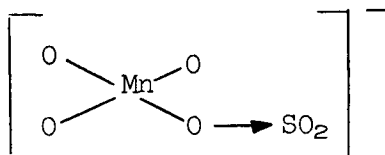
Recent work[14] carried out on the leaching of manganese dioxide with sulphurous acid also suggests that undissociated sulphur dioxide molecules can enter into the reaction. In fact it is suggested that these neutral molecules react more quickly than charged bisulphite ions at active sites on the manganese oxide surface.

Summary of the reactions of the iron (III)-sulphur IV System

The reactions that are thought to take place in the ferric iron-sulphurous acid system are summarised in the following paragraphs. It must be emphasized that these reactions have been proposed as a result of studies which were all carried out at room temperatures, and the majority carried out in homogeneous systems:

i) The first step involves the production of a thionate free radical (HSO_3). This may result from the formation and subsequent decompositon of a ferric-bisulphite complex ion which is a stable species,

$$Fe^{+++} + HSO_3^{-} \rightleftharpoons Fe(HSO_3)^{++}$$
$$Fe(HSO_3)^{++} \longrightarrow Fe^{++} + HSO_3$$
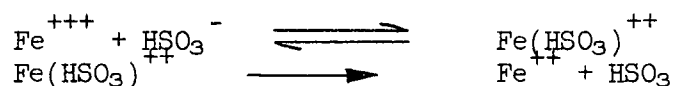
or may be produced directly by the reaction of ferric ion with bisulphite ion

$$Fe^{+++} + HSO_3^{-} \longrightarrow Fe^{++} + HSO_3$$
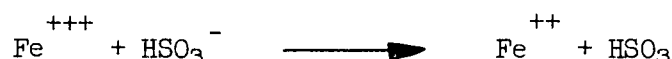
ii) The thionate radical may disappear by one or more of the following reactions:

a) Back reaction with ferrous ion

$$Fe^{++} + HSO_3 \longrightarrow Fe^{+++} + HSO_3^{-}$$
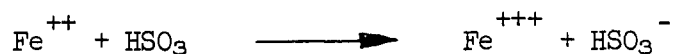
b) Dimerisation to form dithionic acid

$$2HSO_3 \longrightarrow H_2S_2O_6$$

c) Reaction with ferric ion and water to form sulphate

$$Fe^{+++} + H_2O + HSO_3 \longrightarrow Fe^{++} + SO_4^{=} + 3H^{+}$$
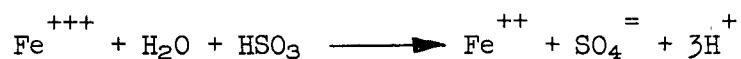
d) In the presence of copper, reaction with cupric ion and water to form cuprous ion

$$Cu^{++} + H_2O + HSO_3 \longrightarrow Cu^{+} + SO_4^{=} + 3H^{+}$$
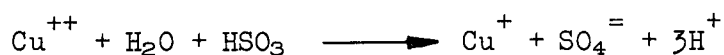
The above reactions assume the formation of a ferric bisulphite complex, but a similar sequence of reactions, resulting in the same end products, may be written involving a ferric sulphite complex and subsequent reactions of the SO_3^{-} radical.

SCOPE OF THE PRESENT INVESTIGATION

The original scope of this investigation was planned to be as follows:-

1) The synthesis and indentification of the two naturally occurring iron oxide hydrates, Goethite (α-FeOOH) and Lepidocrocite (γ-FeOOH).

2) The preparation of bulk compacts of the synthetic oxide hydrate powders suitable for leaching.

3) A study and comparison of the dissolution of the two hydrated oxides in acidified solutions of sulphur dioxide, at elevated temperatures and pressures.

The first part of the investigation was completed successfully. However it was found impossible to prepare compacts of the synthetic powders which had enough cohesion to prevent disintegration during leaching. Because of this, it was decided to study the dissolution of naturally occurring massive hydrated α-iron oxide. The study had to be limited to the α-form of the oxide, since the γ-form very rarely occurs naturally in pure massive form, α-iron oxide hydrate usually being found with it.

Although the synthesis and identification of the oxides now has no bearing on the main part of this work, i.e. the dissolution study, it is included in the first part of this thesis for the sake of completness, and also as a reference in the event that any further work is to be carried out using these synthetic materials.

Thus this thesis is divided into two parts, complete in

themselves. The first part deals with the synthesis, indentification, and preparation of compacts of the hydrated oxides. The second part, which constitutes the bulk of the work carried out, deals with the dissolution of the natural mineral, Goethite, in acid solutions and in acidified solutions of sulphur dioxide.

PART I

The Synthetic Iron Oxide Hydrates

There are two naturally occuring iron oxide hydrates, Goethite and Lepidocrocite. The synthetic materials corresponding to these two minerals are respectively α-FeOOH and γ-FeOOH. α-FeOOH may be regarded as a hydrated form of hematite, α-Fe$_2$O$_3$, and γ-FeOOH as a hydrated form of maghemite, γ-Fe$_2$O$_3$.

This part of the thesis deals with the work done on these synthetic iron oxide hydrates and is reported under the following sections:

1) Preparation of the iron oxide hydrates

2) Identification of the iron oxide hydrates

3) Preparation of leaching specimens.

1) Preparation of Iron oxide hydrates.

Review of Methods

α -FeOOH

There are three general methods of preparing α -FeOOH:

   i) By the oxidation of ferrous compounds in aqueous solution

  ii) By the slow hydrolysis of some ferric salts

 iii) By the aging of brown or yellow gels

i) Oxidation of ferrous compounds

Rapid oxidation by the passage of air through solutions of ferrous chloride[12] or ferrous carbonate, formed by the addition of sodium or ammonium carbonate to ferrous chloride solutions[15], produces α-FeOOH. This can also be achieved by the oxidation of ferrous hydroxide solution with oxygen[16], or air[17]. A more highly hydrous form may be prepared by the rapid oxidation of ferrous bicarbonate solution with peroxide, oxygen, or air at room temperature. This hydrous material will lose its excess moisture and become α-FeOOH if heated in a stream of dry air at 100°C for 48 hours[18].

ii) Slow hydrolysis of ferric salts

The hydrolysis of solutions of ferric salts, such as nitrate, sulphate, acetate, bromide and oxalate gives either α-FeOOH or α-Fe$_2$O$_3$ depending on the conditions[19]. At room temperature the rate of hydrolysis is slow, solutions requiring several weeks to become completely hydrolysed. Hydrolysis is more rapid at higher tempratures, but α-Fe$_2$O$_3$ is formed instead of α-FeOOH if the solutions are boiled[20]. The concentration of ferric salt also affects the product. In general, it is not possible to

obtain pure α-FeOOH from highly concentrated solutions[20]. α-FeOOH can also be prepared from ferric hydroxide, freshly precipitated from ferric nitrate solution, by adding it to 2N KOH solution and then passing in steam[21,22].

iii) <u>Aging of the brown or yellow gels</u>

The brown gel, $Fe_2O_3nH_2O$, prepared by the direct neutralisation of a ferric salt with an alkali hydroxide, when aged in air for a period of about two years, gives α-FeOOH. Aging of the yellow gel, $Fe_2O_3nH_2O$, prepared by the oxidation of freshly precipitated ferrous carbonate with hydrogen peroxide, for a period of a week gives α-FeOOH[23].

<u>γ-FeOOH</u>

The most widely used method of preparing pure γ-FeOOH is the addition of a complexing agent, such as pyridine, soduim azide, or urotropin, to a solution of ferrous chloride. This solution is then oxidised with air or a solution of sodium nitrite[15,19,21,22,24]. Other methods of preparation of γ-FeOOH are by the oxidation of a ferrous salt solution with equivalent amounts of sodium iodate and sodium thiosulphate[24,25] and by the oxidation of freshly prepared hydrous Fe_3O_4[19], hydrous $3Fe_2O_3 \cdot 2FeO$[26], Fe_2S_3 and FeS[27].

<u>Experimental</u>

<u>Preparation 1 - α-FeOOH</u>

$(NH_4)_2CO_3$ (96g) was dissolved in water (1 litre). $FeSO_4 \cdot 7H_2O$ (278g) was dissolved in water (2 litre). A few drops of concentrated sulphuric acid were added to the sulphate solution to produce a clear

blue-green solution. The slight brown residue was filtered off. The ammonium carbonate solution was added dropwise to the sulphate solution at room temperature over a period of about 8 hours (approximately 30 drops per minute). During this time the solution was agitated and a rapid flow of air was maintained through it. The orange-brown precipitate was filtered off, washed with water and dried at 60°C. The yield was 61.5% of the theoretical amount.

Preparation 2 - α-FeOOH

A solution of potassium hydroxide (363.6gm) in water (500ml) was added to a solution of $FeSO_4 \cdot 7H_2O$ (200gm) in water (3 litre). The solutions were pre-heated to 70°C before mixing. The mixture was kept at 70°C and oxidised by bubbling air through the agitated solution for 2 1/2 hours. During oxidation the precipitate turned from a blue-grey to a yellow-ochre colour. After oxidation the precipitate was filtered, washed with distilled water and dried at 60°C. The yield was 95% of the theoretical amount.

Preparation 3 - γ-FeOOH

Pyridine (500ml) was slowly heated to its boiling point and then allowed to cool to room temperature in a carbon dioxide atmosphere. Pure ferrous chloride solution (125ml), which had stood over powdered iron to remove excess acid, was added dropwise while a current of carbon dioxide was maintained through the apparatus. A yellow crystalline precipitate of tetrapyridine ferrous chloride (T.F.C.) was formed.

$$FeCl_2 + 4C_5H_5N \longrightarrow Fe(C_5H_5N)_4Cl_2$$
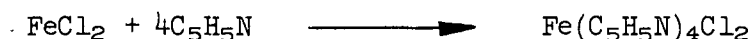
The solution was allowed to stand for one hour under a carbon dioxide atmosphere. The T.F.C. was filtered off and dissolved in water (3 litre), forming a dark brown-green solution. Air was then bubbled through this solution, slowly for 15 minutes and then rapidly for 30 minutes. A yellow-brown precipitate was formed, which was filtered off, washed, and dried at 60°C.

Yield = 3.03 gm.

Preparation 4 - γ-FeOOH

Pyridine (20ml) and water (100ml) were added to saturated ferrous chloride solution (100ml). The solution was agitated and air was passed through rapidly for 30 minutes. A red-brown precipitate was formed, which was filtered off, washed, and dried at 60°C.

Yield = 3.50 gm.

Preparation 5 - γ-FeOOH

Ferrous chloride (80gm) was dissolved in water (2 litre) and the solution was filtered. Urotropine (Hexamethylenetetramine) (112gm) was dissolved in water (400ml) and filtered. The Urotropine solution was added to the ferrous chloride solution. A solution of sodium nitrite (28gm) in water (400ml) was added dropwise with constant stirring. The solution was then heated to 60°C and held at this temperature for 30 minutes, with occasional stirring. A red-brown precipitate formed during heating. Gas was evolved as the temperature reached 60°C. After 30 minutes, the solution was allowed to cool. 3 hours after the beginning of the heating, the red-brown precipitate was filtered off, washed until no chloride was present in the filtrate, and then dried at 60°C. The yield was 62% of the theoretical amount.

2) Identification of the Iron oxide hydrates.

Attempts were made to positively identify the products of the preceding syntheses by the use of 3 different analytical techniques, namely: Infra-red absorption analysis

Differential thermal analysis

X-ray diffraction

The results obtained using each of these three techniques are reported and discussed in the next three sub-sections.

Infra-red absorption analysis.

A review of the literature indicated that infra-red absorption analysis could be used to distinguish between the isomeric forms of FeOOH. The spectra of all the synthetic preparations and of samples of the natural minerals were determined.

The bonds in the FeOOH molecule are the Fe-O bond and the O-H bond. However, there is also hydrogen bonding between hydroxyl groups and oxygen atoms of different molecules, O-H....O. The iron-oxygen bonding was studied by Bass and Benedict[28], and its absorption spectrum was found to lie in the range 7000-15000 cm^{-1}, which is outside the range used in this investigation. The wavelength range studied in this work lay between 600 and 4000 cm^{-1}. The absorption bands of the hydroxyl and hydroxyl-oxygen bonds occur within this range.

A hydroxyl bond with no associated hydrogen bonding shows a sharp absoprtion peak at about 2.75μ, due to stretching vibrations along the bond axis. The stretching vibration of the hydroxyl group is commonly symbolised by ν-OH. As the hydrogen bonding between the

hydroxyl group and the neighbouring oxygen atom becomes stronger, the

ν-OH peak becomes broader and weaker, and the frequency shifts to lower

values.

If the hydroxyl-oxygen hydrogen bond has a strength comparable

to the hydroxyl bond itself, then it should be possible to observe an

absorption due to the bending vibrations of the O-H····O group. (See Fig. 1).

In plane bending
or scissoring

Out of plane bending
or wagging

FIGURE I   Bending vibrations of the OH····O group

Absorptions due to bending vibrations are observed in

compounds with strongly hydrogen bound hydroxyl-oxygen groups in the

range 800-1100cm^{-1}.   The symbol for bending vibrations of this group is

δ-OH.

Several workers have studied the infra-red absorption spectra

of Goethite and Lepidocrocite[22,29,30,31,32,33]. The reported band

frequencies are as follows:-

	ν-OH (cm^{-1})	δ-OH (cm^{-1})
Goethite	3049-95	885 and 797
Lepidocrocite	3120	1025

It may be seen that δ-OH in Goethite is reported as giving

rise to a double absorption band, whereas in Lepidocrocite it gives

only a single band.

Sample	Wave Number cm^{-1}						
Natural Goethite*	3800 - 2800 b.w.		1100 v.w.		895 s.	795 s.	
Natural Lepidocrocite*	3200 - 2800 b.w.	1640 b.w.	1160 w.	1025 w.	890 w.	790 m.	
Preparation 1 (α-FeOOH)	3160 b.s.	1630 b.w.	1135 m.	1020 m.	885 s.	795 s.	
Preparation 2 (α-FeOOH)	3140 b.s.	1640 b.w.			895 s.	795 s.	
Preparation 3 (γ-FeOOH)	3050 b.s.	1620 b.w.	1155 b.w.	1020 s.			750 m.
Preparation 4 (γ-FeOOH)	3440 b.s.		1155 v.w.	1020 m.			
Preparation 5 (γ-FeOOH)	3000 - 2800 b.s.		1160 w.	1020 w.			

* Purchased from Wards

KEY: b.w. = Broad and weak   w. = Weak
      b.s. = Broad and strong   m. = Medium
      v.w. = Very weak   s. = Strong

Table 1 Infra-red absorption spectra of natural and synthetic iron oxide hydrates

Results

The samples were prepared for analysis both as KBr pellets and as Nujol mulls with equal success. The frequencies of the observed absorption bands are reported in Table I.

It may be seen that the infra-red absorption spectra of the natural and synthetic samples of FeOOH can be grouped into distinct sets of bands. These bands are indicated by the dotted lines in Table I.

$3000cm^{-1}$ range: These bands, which were evident in every sample, were very broad, and the peak frequencies somewhat scattered.

$1600-1650cm^{-1}$ range: These bands are broad and weak and are evident in only three of the synthetic materials and one of the natural minerals. Absorption at this frequency is attributable to adsorbed water[30].

$1160-1000cm^{-1}$ range: In this range a double band is evident in all but the natural goethite and one of the synthetic α-FeOOH preparations (Prep. 2). The double band has a weak peak at approximately $1150cm^{-1}$ and a fairly strong peak at $1020cm^{-1}$.

$790-900cm^{-1}$ range: A second double band, with peaks at ~ 890 and $795cm^{-1}$, is present in the two natural minerals and the two synthetic α-FeOOH preparations. These bands are strong in the natural goethite and the synthetic materials, but weak in the natural lepidocrocite.

Discussion

The broad bands found in the $3000cm^{-1}$ range are attributable to ν-OH, and the broadness is caused by strong hydrogen bonding. The

broadness of these bands was greater in the natural minerals than in the synthetic materials, indicating that the hydrogen bonding is stronger in the former than the latter.

The double bands in the range 1150-790cm^{-1} may be attributed to the bending vibration, δ-OH, of the O-H····O group[29,30,33,34]. The double band at 890 and 795cm^{-1} is very characteristic of α-FeOOH. It is not known why this band should show two peaks. Glemser and Hartert[34] consider that it is a consequence of the rhombic crystal structure of goethite, since α-AlOOH, α-GaOOH, and $\mathcal{E}$-Zn(OH)$_2$, which are all rhombic, all give double bands in this range, whereas the non-rhombic In(OH)$_3$ gives only one band.

The δ-OH vibration in Lepidocrocite is reported in the literature as giving rise to only one band at 1020cm^{-1}. It may be seen from the results, that the present investigation has shown that two peaks occur in this region, a strong peak at 1020cm^{-1} and a weak peak at approximately 1150cm^{-1}. It is suggested that this second peak is also due to δ-OH of Lepidocrocite, for the following reasons:

    i) Lepidocrocite has a rhombic crystal structure

    ii) Böhmite (γ-AlOOH), which is isomorphous with Lepidocrocite, shows a double band with peaks at 1145 and 1073cm^{-1} [35].

Conclusions

    i) The results obtained in this investigation for the infra-red absorption spectrum of Goethite (α-FeOOH) agree with those reported in the literature. The spectrum for this material consists of a broad,

rather undefined band in 3500-3000cm^{-1} range due to ν-OH with associated hydrogen bonding, and two strong, well-defined peaks at 890 and 795cm^{-1}, due to δ-OH.

    ii) The absoprtion spectrum of Lepidocrocite (γ-FeOOH) is similar to α-FeOOH in the 3000cm^{-1} range, but it shows a strong peak at 1020cm^{-1} and a weak peak at approximately 1150cm^{-1}. Both these peaks are thought to be due to δ-OH.

    iii) The broadness of the ν-OH peaks is greater in the natural minerals than in the synthetic materials, indicating stronger hydrogen bonding in the former materials.

    iv) The natural goethite sample contains virtually pure α-FeOOH, as does preparation 2.

    v) The natural lepidocrocite sample and preparation 1 contain mixtures of α- and γ-FeOOH.

    vi) Preparations 3, 4, and 5 contain pure γ-FeOOH.

    vii) Infra-red analysis is a good method for distinguishing between the isomeric forms of iron oxide hydrate.

ii) Differential Thermal Analysis

    Since goethite and lepidocrocite, α-FeOOH and γ-FeOOH, have different crystal structures, it should theoretically be possible to distinguish between them by differential thermal analysis. On heating, goethite dehydrates directly to hematite, α-Fe$_2$O$_3$, whereas lepidocrocite first dehydrates to maghemite, γ-Fe$_2$O$_3$. At a higher temperature γ-Fe$_2$O$_3$

transforms to α-Fe_2O_3. In most cases, these differences are apparent by D.T.A. The D.T.A. curve for goethite consists of a single endothermic peak occurring between 385-400°C[18,37,38]. The curve for lepidocrocite is reported to consist of an endothermic peak occurring about 350°C, followed by a variable exothermic peak, usually at about 450°C[37,38]. The particle size is known to affect the temperatures of these transformations, with a decrease in particle size lowering the transformation temperatures. The above mentioned figures are for coarsely crystalline materials. Paticle size can cause the peaks to vary between 300-400°C for goethite[36], and 300-360°C for the endothermic, and 370-450°C for the exothermic transformations of lepidocrocite[37].

A difficulty arises when trying to distinguish between poorly crystallised goethite and lepidocrocite. Poorly crystallised goethite is said to dehydrate first to amorphous Fe_2O_3, which then crystallises to α-Fe_2O_3, producing an exothermic peak on the curve. This type of curve can be easily confused with the lepidocrocite-type curve[23,39].

Results

The temperatures at which peaks were observed in the D.T.A. curves of the various samples may be found in Table 2.

Sample	Temperature (°C)
Natural Goethite*	440 (Exo)
Natural Lepidocrocite*	400 (Exo)
Preparation 1 (α-FeOOH)	320 (Endo) 670 (Exo)
Preparation 3 (γ-FeOOH)	210 (Exo) 275 (Endo) 440 (Exo) 592 (Exo)
Preparation 4 (γ-FeOOH)	285 (Endo) 415 (Exo)
Preparation 5 (γ-FeOOH)	285 (Endo) 430 (Exo)

Table 2: D.T.A. curves for natural and synthetic iron oxide hydrates

* Purchased from Wards

Conclusions-

i) The sample of so-called natural lepidocrocite appears to consist mainly of goethite

ii) Preparation 1 could be lepidocrocite, γ-FeOOH

iii) Preparations 4 and 5 give curves in reasonable agreement with the reported values for lepidocrocite

iv) For the purposes of this investigation, D.T.A. is not a conclusive method of identifying the synthetically prepared iron oxide hydrates.

iii) X-ray Diffraction

Since it had been shown that the two isomers α- and γ-FeOOH

could be readily distinguished by their infra-red absorption specta, only a very limited X-ray investigation was carried out.

The major peaks in the reported X-ray diffraction patterns are listed in Table 3. The relative intensities reported by different sources show considerable variation, but there is general agreement on the θ values of the peaks.

Synthetic α-FeOOH (Prep. 2) and γ-FeOOH (Prep. 4) were examined. The results may be found in Table 4. The peaks in the diffraction patterns of these materials were rather broad, but it is thought that reasonable agreement is shown between the θ values of the synthetic materials and the reported values.

General Conclusions on the preparation and identification of the iron oxide hydrates:

1) Infra-red absorption analysis is a good technique for distinguishing conclusively between the isomeric forms of iron oxide hydrate.

2) Pure α-FeOOH may be synthesised by Preparation 2.

3) Pure γ-FeOOH may be sythesised by Preparations 3, 4, and 5. Preparation 5 was found to give the highest yield of material.

Table 3: Major peaks of X-ray diffraction patterns of α-and γ-FeOOH (ASTM card index)

	α-FeOOH			γ-FeOOH		
d Å	θ	I/I_m		d Å	θ	I/I_m
5.00	11.2	60		6.26	8.9	100
4.21	13.3	100		3.29	17.1	90
2.69	21.2	70		2.47	23.1	60
2.58	22.0	20		1.94	29.9	70
2.44	23.4	80				
1.72	34.3	50				

Table 4: X-ray diffraction patterns of the synthetic materials

	α-FeOOH (Prep. 2)			γ-FeOOH (Prep. 4)		
d Å	θ	I/I_m		d Å	θ	I/I_m
4.98	11.2	20		6.34	8.8	90
4.20	13.3	100		3.31	17.0	100
2.70	21.0	30		2.48	23.0	80
2.58	22.0	20		1.94	29.9	70
2.46	23.2	60				
1.72	34.3	30				

3. Preparation of Leaching Specimens

In order to prepare samples of the synthetic materials suitable for leaching, tests were carried out to determine the suitability of the powders for compacting, machining, and cutting. This was followed by tests on the prepared samples under autoclave conditions.

Compacting

A bulk preparation of α-FeOOH (Preparation 1) was made, and the tests carried out with this powder. Three types of compactions were tried -

a) 18 gm of powder were hydrostatically compressed in oil, enclosed in a rubber tube, to a pressure of 35000 psi. The cohesion of the compact was good and its density was 2.20 gm/cc, 53% of theoretical.

b) 16 gm of powder were statically compressed to a pressure of 117,000 psi. The density of this compact was slightly greater, 2.56 gm/cc, 61.5% of theoretical, but it was more brittle than (a).

c) A statically compressed billet was crushed to pass a 16 mesh screen and recompressed statically to 117000 psi. The density of the material was 2.64 gm/cc, 63.5% of theoretical, but the cohesion of the billet was poor.

Machining, cutting and mounting

It was found possible to machine the hydrostatically pressed billets to round section, using a standard metal-working lathe at slow speed and slow horizontal movement of the tool.

The billets were sliced into sections, using a jeweller's saw with a very fine blade. A small jig was used to hold the billet and to guide the blade vertically during cutting. Sections of the compacts were mounted in epoxy resin with one surface exposed. The exposed face was then ground flat.

Specimen Testing

Mounted sections, prepared in the above manner, were tested to determine whether they would withstand typical pressure leaching conditions. Initially, tests with these specimens were successful, no cracking or disintegration of the compacts being observed. However after a period of a few weeks, specimens prepared in an identical manner to the earlier ones began to disintegrate during leaching. It was found impossible to prevent this. The reasons for this disintegration are not known, but it is conjectured that the iron oxide hydrate powder underwent some aging process which sufficiently changed its surface properties to reduce the cohesion of the compacts.

It was undesirable to work with freshly prepared oxide powders because there was no guarantee that the leaching characteristics of one batch would be the same as another, and so it was decided to abandon the idea of working with synthetic material and use naturally occurring massive goethite.

Part II of this thesis deals with the work carried out using this material.

PART II

The Dissolution of Natural α-Iron Oxide

Hydrate in Aqueous Solutions of Sulphur Dioxide

EXPERIMENTAL

Materials

(a) Reagents: Reagent-grade chemicals were used exclusively.
Nitrogen and sulphur dioxide were supplied by Matheson Co. and used
without further purification.

(b) Natural mineral: A quantity of massive natural
goethite was purchased from Ward's Natural Science Establishment. Wet
chemical analysis showed that the mineral contained 56% iron, indicating
an FeOOH content of 89 %. Infra-red absorption analysis showed that the
iron oxide hydrate content of the mineral was pure α-FeOOH. A
qualitiative spectrographic analysis indicated that silicon was the major
impurity, some aluminium was present, also traces of sodium, manganese,
titanium, copper, nickel and cobalt (See Table 5). The X-ray diffraction
pattern of the mineral showed good agreement with the reported pattern
for goethite (See Table 6). The major peak for silica was also observed.

Table 5:   Qualitative spectrographic examination of natural goethite

Iron	Major Constituent	+10%
Silicon	Intermediate Constituent	+1%
Aluminium	Minor Constituent	Approx. 1%
Sodium Manganese Titanium Copper	Traces	Approx. 0.01%
Nickel Cobalt		Approx. 0.001%

Insolubles Approximately 10%

Table 6: . X-ray diffraction pattern of the natural goethite

Reported			This study		
d $\overset{o}{A}$	θ	I/I_m	d $\overset{o}{A}$	θ	I/I_m
5.00	11.2	60	5.03	11.1	20
4.21	13.3	100	4.21	13.3	100
2.69	21.2	70	2.70	21.0	30
·2.58	22.0	·20	--------		
2.44	23.4	80	2.46	23.2	25
1.72	34.3	50	1.72	34.2	15

Initially the mineral was cut on a diamond saw into rectangular blocks, and mounted in epoxy resin with one face exposed. The exposed face was ground flat and used as the leaching specimen. This method of specimen preparation was found to be unsatisfactory due to poor reproductibility of results amongst different specimens. The lack of reproducibility was thought to be due to either one, or both of the following reasons:

a) Inhomogeneous dispersion of impurities in the mineral

b) Preferential leaching along certain crystal planes.

In order to overcome these inhomogenieties of the mineral, it was decided to work with a particulate feed.

The mineral was crushed into small pieces with a sledge-hammer, and then ground down to the required size using a hand-muller. The particles were sized by wet screening to remove adhering fines. The -65 + 150 mesh fraction was chosen and used for all leaching tests. After screening and drying, particles of iron from the grinding tools were removed with a hand magnet.

Leaching was carried out on weighed samples of this material. Either one or two gram samples were used. Sampling was done using a 7-point technique, and the bulk material was rolled on a polythene sheet during sampling to ensure complete mixing. The surface area of the particle feed used was estimated to be $90cm^2/gm \pm 30\%$.

Autoclave Design

A 1 litre stainless steel (316SS) autoclave with a glass

liner was used. Baffles, consisting of four glass rods set at 90° to one another, were held in place against the sides of the liner by two annular Teflon rings. Stirring was provided by a Magnedrive unit, supplied by Autoclave Engineers. This unit had a completely enclosed stirring shaft, which was actuated by means of an external rotating magnet. The gas inlet tube, of 1/8" copper tubing, was attached to the top of the stirrer shaft housing. This housing was made of 316ss. Sulphur dioxide, nitrogen, or compressed air could be delivered through the inlet tube. The stainless steel stirring shaft was sheathed by Teflon rod, drilled to give a snug fit over the shaft. Agitation was provided by a Teflon block which was threaded on to the bottom of stirrer shaft sheath. The stirring speed used for all runs was 900 R.P.M. Visual tests showed that this stirring speed, plus the effect of the baffles, provided extremely turbulent agitation of the solution.

The inside face of the stainless steel head was covered by Teflon sheet, which was bonded to the steel surface. The thermistor well was of copper, covered with Tygon paint and sheathed with Tygon tubing. The sample tube inside the autoclave was of polyethylene with a sintered glass filter fitted on the inlet end of the tube. The external part of the sample tube was of 1/8" copper tube, and the sample valve constructed from Beryllium-copper. The gas exit line was 1/4" 316ss tubing. The pressure gauge, 0-100 psi Duragauge 316ss Type, was connected to the gas exit tube, on the pressure side of the exhaust valve. Heating was provided by a circular gas burner controlled by a solenoid valve. This valve was activated by a Thermistemp temperature controller (Yellowsprings Instrument Co.) The temperature of the contents of the

autoclave was measured by a high temperature thermistor probe, inserted into the thermistor well. Using this system, the temperature was controlled to within $\pm$ 1.5°C.

Experimental Procedure

The experimental procedure consisted of the following steps:

i) A one or two gram sample of mineral, reagents, and sufficient water to give a solution volume of 655ml were put into the autoclave.

ii) The vessel was sealed and the stirrer started.

iii) The exhaust valve was opened and nitrogen was allowed to flush through the vessel for the whole of the warm-up period.

iv) The solution was allowed to boil under the nitrogen atmosphere for 10-15 minutes, in order to displace any dissolved oxygen.

v) The exhaust valve was then closed down until there was just a small bleed of gas escaping from the vessel. This bleed was continued throughout each run.

vi) Heating was resumed. When the solution was a few degrees below reaction temperature., the nitrogen supply was turned off and sulphur dioxide was introduced at the required pressure.

For runs carried out in the absence of sulphur dioxide, i.e. the direct dissolution experiments, a nitrogen atmosphere was maintained throughout the run.

vii) The solution was allowed to stabilise at the reaction temperature (usually about 10 minutes after the introduction of the

sulphur dioxide), and the first sample was taken. The concentration of iron in this sample was used as the blank for the calculation of the rate curve for the run.

viii) Samples for iron determination were taken at regular intervals throughout a run, usually six samples per run. Sampling procedure involved first taking and discarding 2 ml of solution. This was to clear the sample tube of unreacted solution. Then a further 5ml sample was taken and used for the iron determination.

ix) Sulphate estimations were carried out on a 100ml sample taken at the end of the run.

The continuous bleed of gas through the system, mentioned in (v) above, was necessary to create a slight excess pressure in the stainless steel head of the autoclave. This excess pressure prevented water vapour from entering the head, and so only dry sulphur dioxide was in contact with the steel. Corrosion of the stainless steel under these conditions was so low that the amount of iron entering the solution from the autoclave during a blank run of 3 hours duration was virtually unmeasurable, and certainly negligible when compared with the rate of leaching of iron from the ore. Water vapour loss through the exhaust valve during a run was negligable.

This technique had the disadvantage that the maximum pressure that could be used in the system was the delivery pressure of the sulphur dioxide. The sulphur dioxide was in liquid form in the delivery tank and so the maximum pressure available was the vapour pressure of liquid sulphur dioxide at ambient temperature. This varied slightly, depending on ambient temperature, but never exceeded 36 psig. Because of this

limitation in the maximum pressure of sulphur dioxide available, the range of acidity and bisulphite ion concentration that could be used in this study was somewhat limited. A system in which higher sulphur dioxide pressures could have been used would have been preferable.

Analytical Methods

a) Iron

The concentration of iron in the sample solutions was measured colorimetrically by means of the orange-red ferrous complex of 1-10-orthophenanthroline. To ensure that all the iron in the solution was in the ferrous state hydroxylamine hydrochloride was used as a reducing agent. The solutions were buffered at pH4.5 with a sodium acetate-acetic acid buffer solution.

A composite reagent was used consisting of 20% by volume of a 0.15% orthophenanthroline solution, 20% by volume of a 1% hydroxylamine hydrochloride solution, and 60% by volume of acetate buffer. 2ml aliquots of sample solution (or smaller, if necessary) were pipetted into 25ml portions of the composite reagent and made up to 100ml with water. The optical density of each solution was measured on a Beckman Model B Spectrophotometer, using light of wavelength 510 mμ. The concentration of iron was read directly from a calibration curve prepared by using standard iron solutions.

b) Sulphate

Sulphate ion was estimated by the method due to Belcher[40]. The sulphate was first precipitated by addition of standard barium

chloride solution. The excess barium chloride was estimated by adding
an excess of standard E.D.T.A. solution. The excess E.D.T.A. was titrated
in alkaline solution with standard magnesium chloride solution, using
Superchrome Black as an indicator. In this way, the poor end-point which
occurs when barium chloride is titrated directly with E.D.T.A. was
avoided.

Because the iron in the solution would complex with the
E.D.T.A. and thus give high results, a modification of the method due
to Hunt[41] was used to remove all cations from the solution. Prior to the
addition of the barium chloride solution, the sample was passed through
a 20cm column of Amberlite 120 Cation exchange resin. The resin was used
in the hydrogen ion substituted state, and when saturated with iron, it
was regenerated by passing through 5N hydrochloric acid solution. This
method was found to be completely successful in removing all measurable
traces of iron from the samples.

Procedure: Sulphate determinations were carried out on a 100ml sample
that was taken at the end of the run. Immediately after withdrawal from
the autoclave, nitrogen was bubbled through the sample for 15-20 minutes
to displace dissolved sulphur dioxide. The sample was then passed slowly
through the ion-exchange column.

A sample (25ml) of the ion-exchanged solution was heated to
boiling. Standard 0.01N $BaCl_2$ solution (20ml) was added and the solution
was allowed to stand for one hour. Standard 0.01M E.D.T.A. solution
(25ml) was then added plus an ammonium chloride-ammonia buffer solution
(20ml). Twelve drops of Superchrome Black indicator were added and the
solution was titrated to a clear cerise-red colour with standard 0.01M
$MgCl_2$ solution. The ammonium chloride-ammonia buffer solution consisted

of 16.5gm NH_4Cl and 226ml concentrated ammonia solution made up to 1 litre, and the Superchrome Black indicator was a 0.5% solution in ethanol. Each sulphate determination was carried out in duplicate or triplicate.

Using the above procedure, it was found possible to measure 1mg of sulphur in standard ferrous ammonium sulphate samples to an accuracy of $\pm$ 2%.

RESULTS

For the sake of clarity the results are presented only as
diagrams accompanying the text in this section. They are presented in
tabulated form in Appendix A. The tables in the appendix follow the
same sequence as the figures in this section.

Direct Dissolution in Acid Solutions

A limited study was carried out to determine the behavior
of goethite in acidic solutions under non-reducing conditions. The
dissolution in perchloric and sulphuric acid solutions was investigated.
1gm samples of the mineral were used in all cases.

Perchloric acid

Dissolution in perchloric acid was found to be very slow. At
130°C and an acid strength of 0.7M, the rate of dissolution was found to
be only 6×10^{-5} moles Fe per hour (See Fig. 6). At lower acidities
and temperatures, the rate was too slow to be accurately measurable.

Sulphuric acid

The effects of acidity and temperature on the dissolution
of goethite in sulphuric acid solutions were studied. Under certain
conditions, namely low acidities and higher temperatures, deviations from
linearity were observed in the plots of concentration versus time
(See Fig. 4). However all rates that are reported have been measured
on the initial linear portions of the concentration plots.

Varying acidity at constant temperature   The effect of

varying the concentration of sulphuric acid in solution at a constant

temperature was investigated. The activity of hydrogen ion at each acid

concentration has been assumed to be equal to the molar concentration of

acid. The rate of dissolution is plotted versus acid concentration in

Fig. 2 and versus hydrogen ion activity in Fig. 3 (Table I Appendix A).

It may be seen that the rate increases approximately linearly with

hydrogen ion activity. The rate of dissolution in sulphuric acid is

faster than in perchloric acid at similar molar concentrations. At

130°C and an acid concentration of approximately 0.7M, the rate of

dissolution in sulphuric acid is of the order of 35 times faster than

in perchloric acid. (See Fig. 6).

Varying temperature at constant acidity   The results for

variations in the temperature at a constant sulphuric acid concentration

may be found in Fig. 4. An Arrhenius plot for these results is given in

Fig. 5 (Table II Appendix A). The slope of this line corresponds to an

activation energy of 18.2 Kcals/mole.

The deviations from linearity of the rate curves at higher

temperatures, evident in Fig. 4, were thought to be due to the fact

that the equilibrium concentration of ferric sulphate was being approached.

In order to substantiate this idea, a run was done in which ferric sulphate

was added to the solution initially. The results of this experiment

are plotted in Fig. 7. 1.9×10^{-4} moles of iron, as ferric sulphate,

were added at the start of this run. It may be seen that the concentration

of iron in solution does approach a maximum value, indicating that the
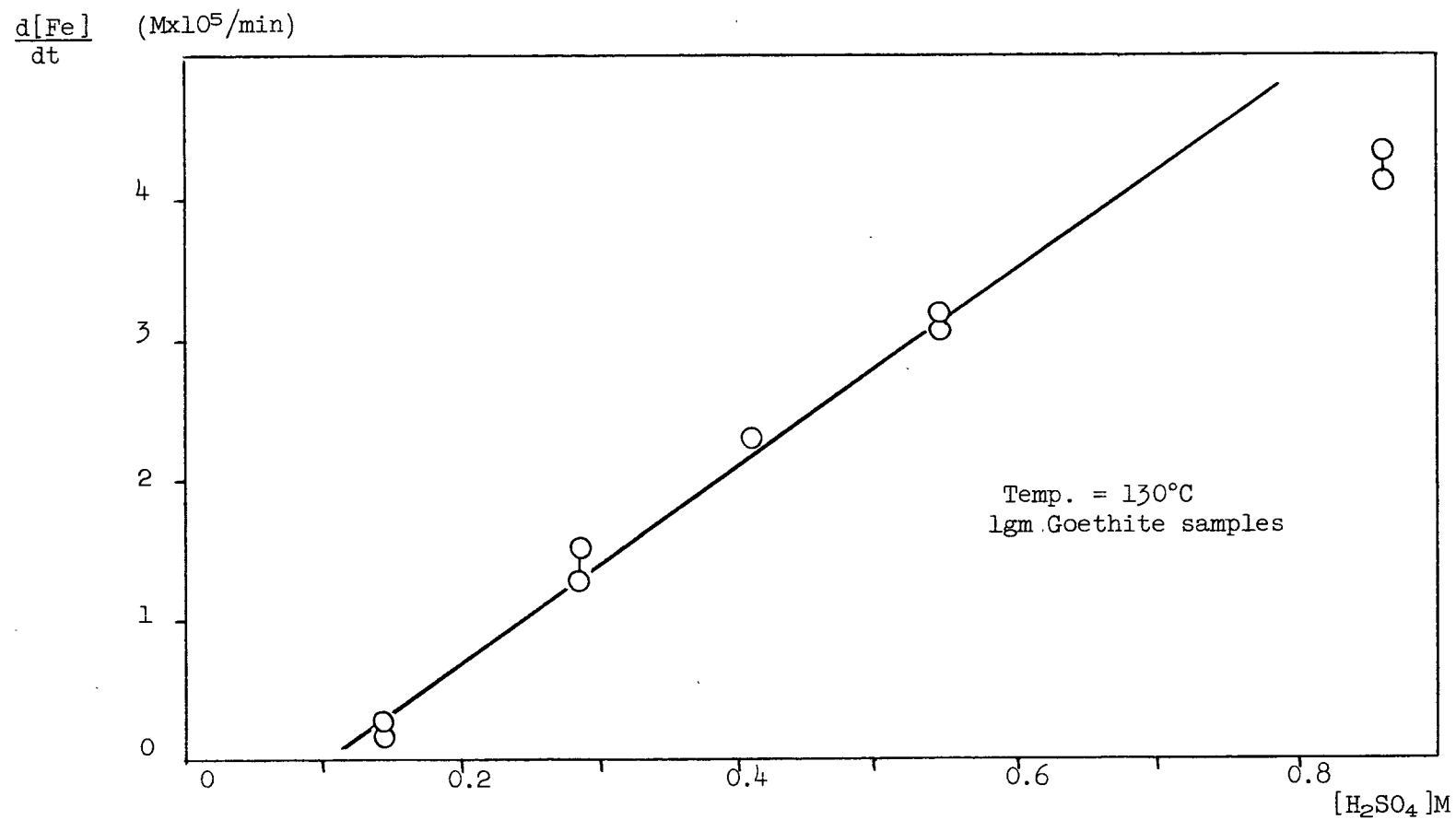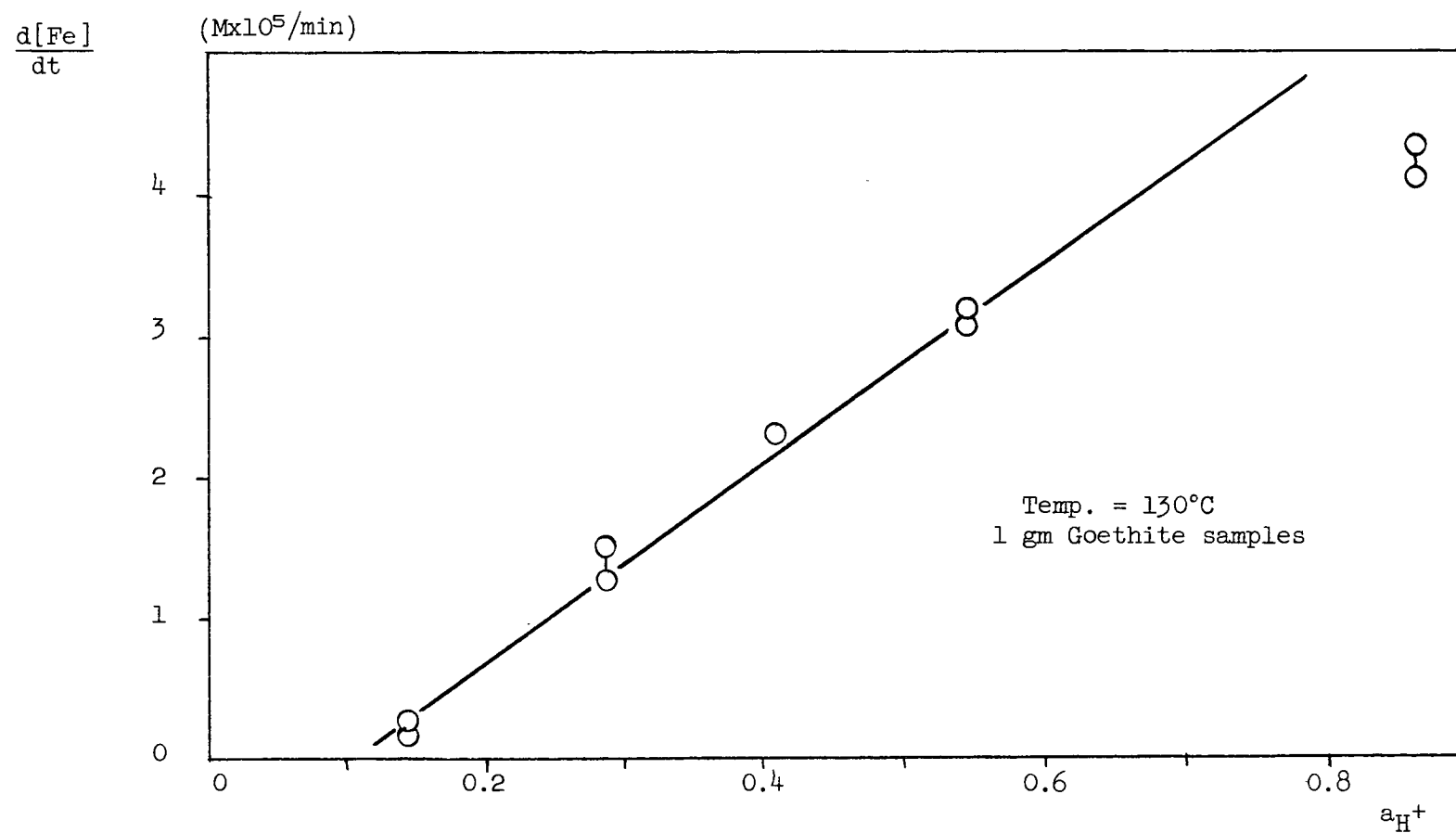
Figure 2   Rate versus concentration of H_2SO_4

Figure 3.   Rate versus activity of hydrogen ion in H_2SO_4
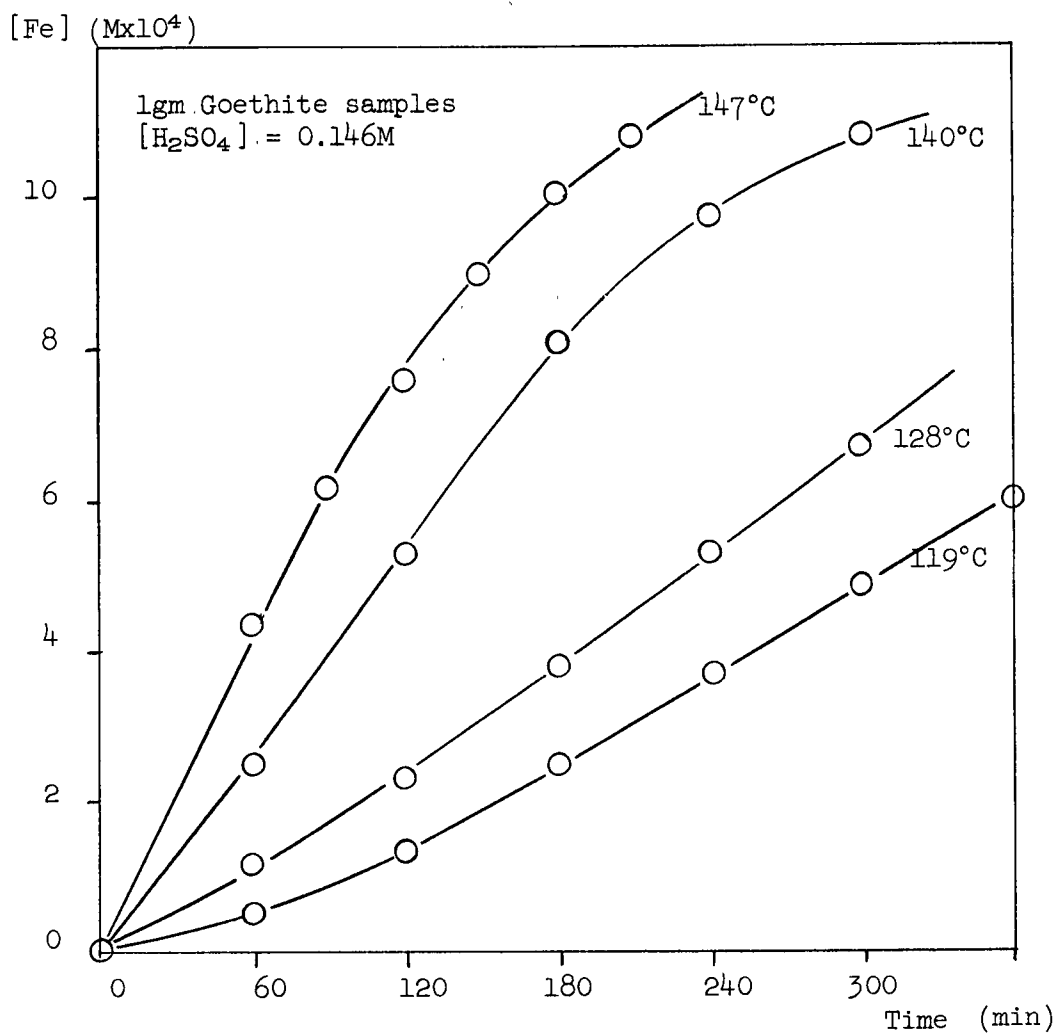
[Fe] (Mx10^4)

lgm Goethite samples
[H$_2$SO$_4$] = 0.146M

147°C

140°C

128°C

119°C

Time (min)

Figure 4. Effect of temperature at constant [H$_2$SO$_4$]
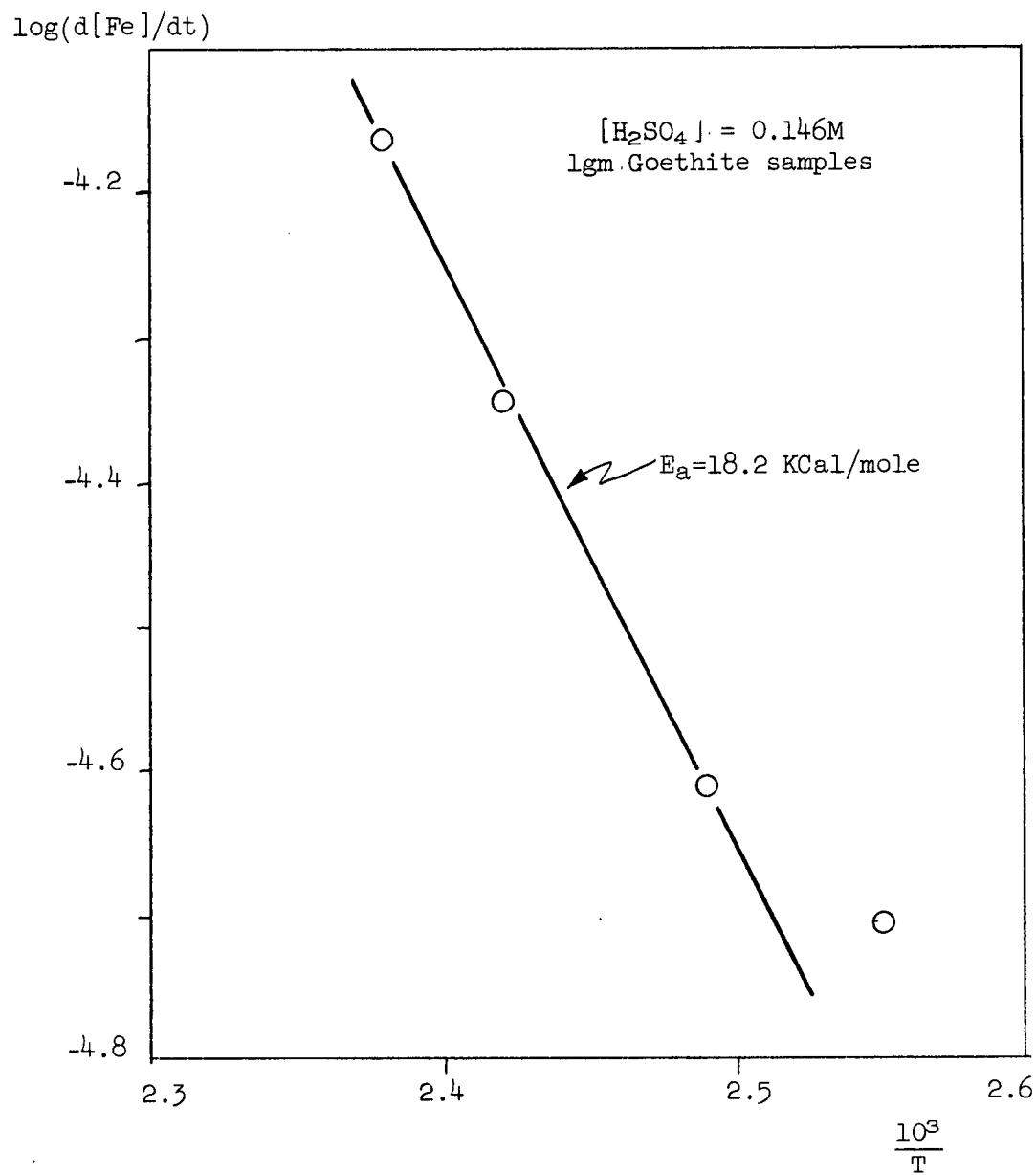
Figure 5.   Arrhenius plot for dissolution in H_2SO_4

[Fe] $(Mx10^4)$

Rate = 21.8 moles $Fex10^4$/hr.

Temp 130°C
● $[H_2SO_4]$ = 0.7M
○ $[HClO_4]$ = 0.7M
  lgm Goethite samples

Rate = 0.6 moles
$Fex10^4$/hr.
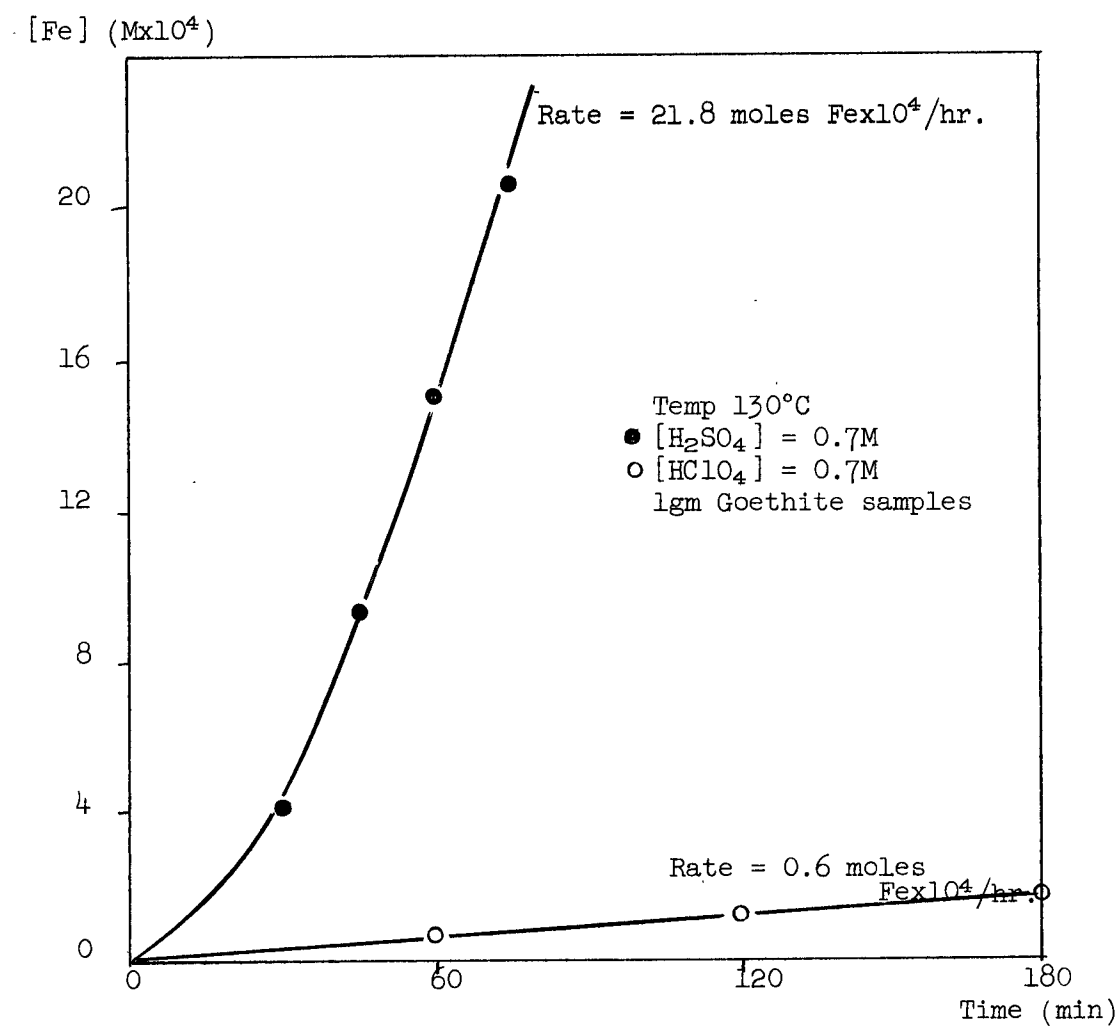
Time (min)

Figure 6 Comparison of rate of dissolution of Goethite in
         sulphuric and perchloric acids
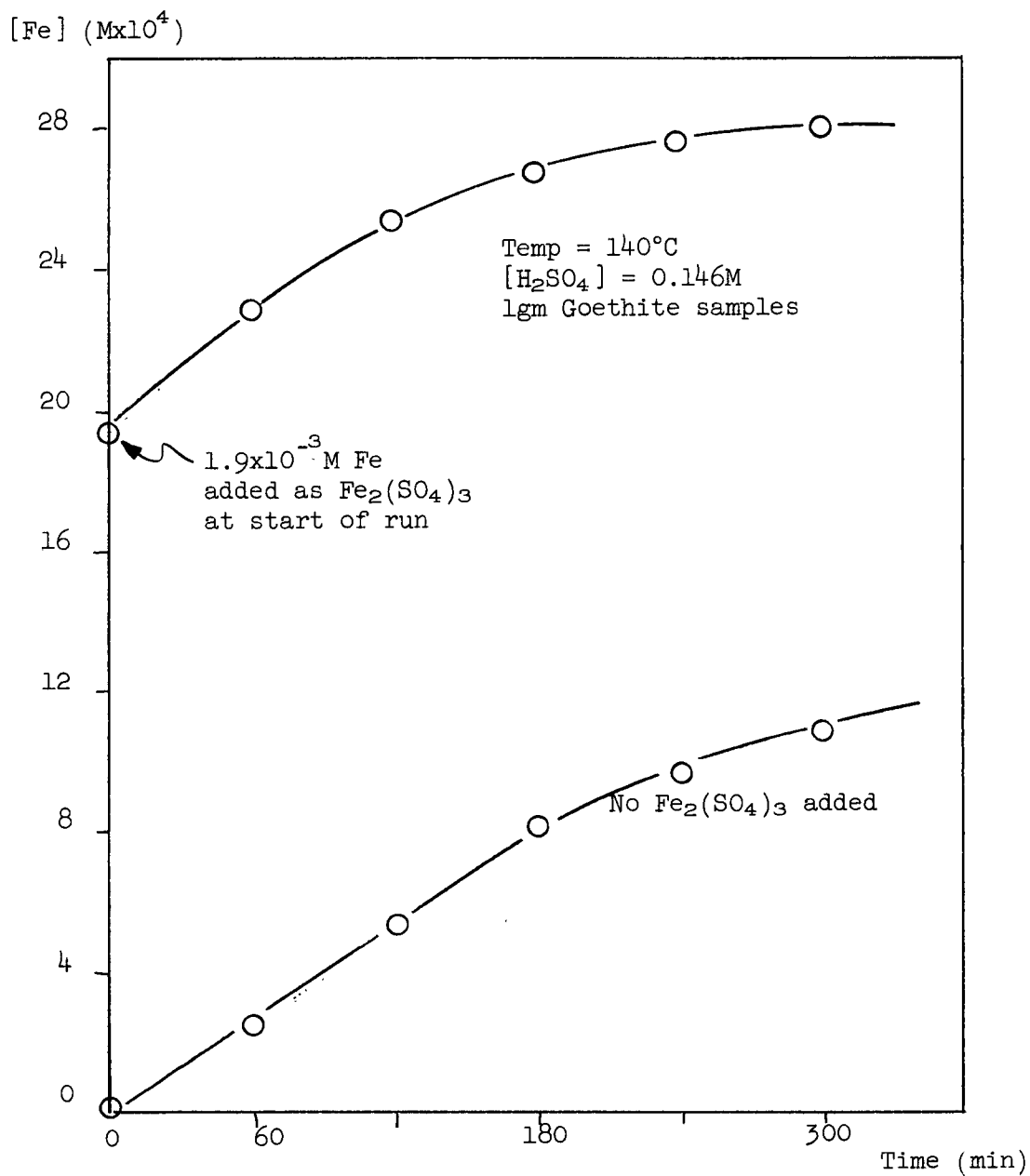
Figure 7 Effect of adding $Fe_2(SO_4)_3$ at the start of the run

·solubility of ferric sulphate may be becoming rate determining. A run carried out under the same conditions, but without the added ferric sulphate, is plotted on the same diagram.

Reductive Dissolution in Acid Solutions

The main body of the leaching experiments was carried out in aqueous solutions of sulphur dioxide, acidified with perchloric acid. A knowledge of the total pressure of the system, the temperature, and the hydrogen ion concentration, enabled the calculation of the concentration of dissolved sulphur dioxide and the concentration of bisulphite ion to be made from the data of Beazley et al[42]. (For a discussion of the sulphur dioxide-water system, and details of these calcuations, see Appendix B.)

Most of these experiments were carried out at a temperature of 110°C. This temperature was chosen for the following reasons:

i) Conveniently measurable rates were obtained.

ii) Sulphur dioxide could only be introduced to the system at pressures above the vapour pressure of water. As the maximum sulphur dioxide pressure available was 36 psi.g., it was desirable to keep the vapour pressure of water, and hence the temperature, as low as possible in order to maximise the range of sulphur dioxide pressures that could be used.

iii) The decomposition temperature of goethite (α-FeOOH) to hematite (α-Fe$_2$O$_3$) in aqueous solutions is variously reported [43,44,45] as occurring between 120-150°C. Thus it was thought preferable to work at a temperature at which goethite would be thermally stable.

One gram samples of the particulate goethite were used for the majority of the runs. However in order to determine areas of heterogeneous and homogeneous control, certain runs were repeated using two gram samples. It may be seen from the following results that these experiments indicated that homogeneous control of the reaction occurred under certain conditions. For this reason, the rates are reported in homogeneous units rather than heterogeneous units. A set of typical rates, observed under conditions of heterogeneous control, and reported in heterogeneous units, may be found in Table X (Appendix A).

Typcial Rate Curves

A set of rate curves, typical of those observed in aqueous sulphur dioxide solutions, may be found in Fig. 8. The shape of these plots ie. a curved portion followed by a linear portion, was characteristic for virtually every run carried out with sulphur dioxide. It was also observed for some of the runs carried out with sulphuric acid solutions. The linear portion began approximately one hour after the start of the run. The curved portion existed for the same time period, ie. the first hour, for all conditions studied, irrespective of the rate of dissolution of iron. Because of this, it was thought to be due to some characteristic of the mineral itself.

The effect of varying the partial pressure of sulphur dioxide at constant acidity

Three series of experiments were done under these conditions at three different perchloric acid concentrations, namely $7.0 \times 10^{-2}M$,
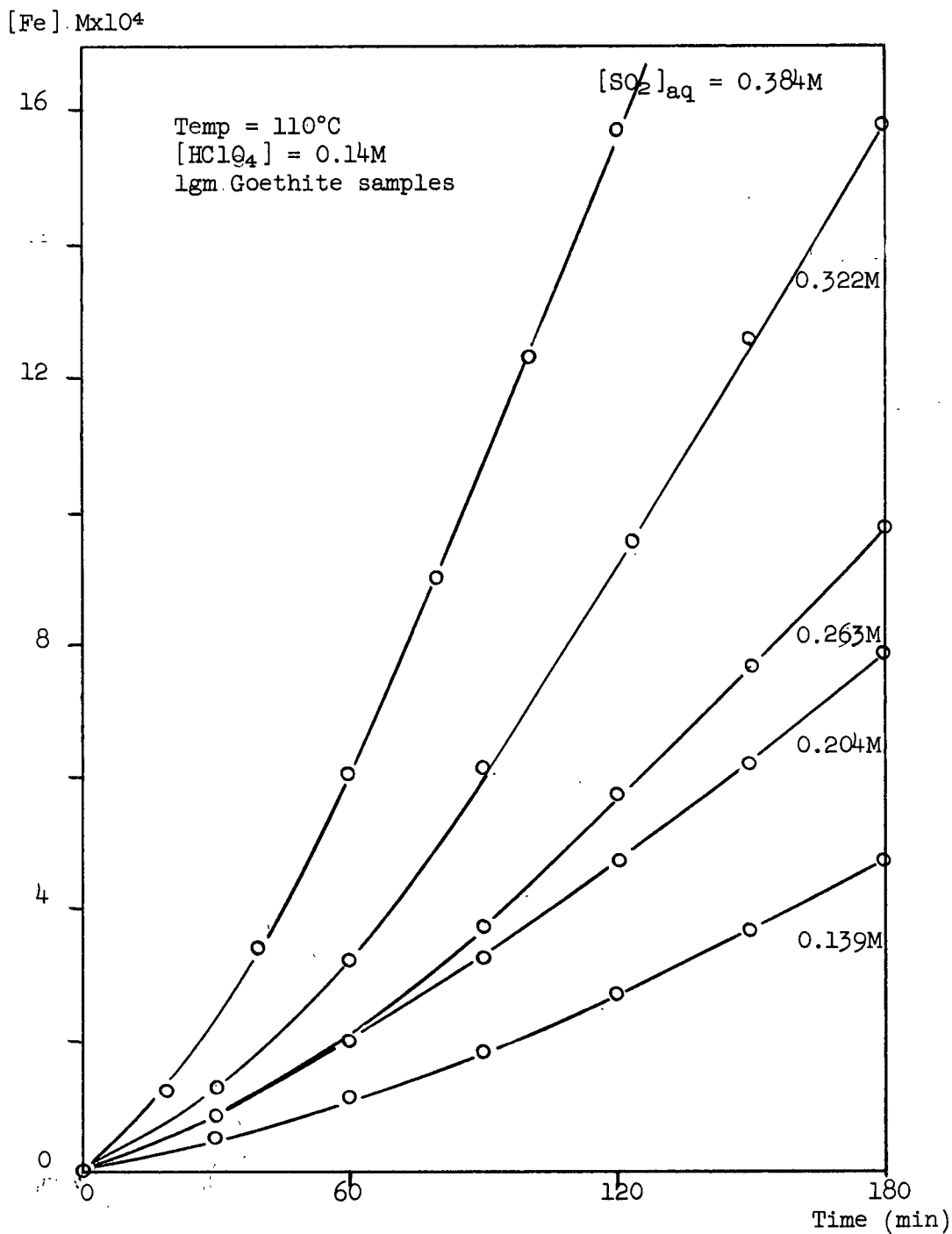
Figure 8 Typical rate plots for dissolution in acidified sulphur dioxide solutions

1.4 x 10^{-1}M and 2.8 x 10^{-1}M. These series are named Series Al, A2 and A3 respectively. The results, as plots of rate of dissolution of iron versus the concentration of dissolved sulphur dioxide for each acidity may be found in Figs. 9, 10, 11. (Table: III Appendix A.)

It may be seen that the curves are all of the same general shape, involving an initially slow increase in rate with sulphur dioxide concentration. This is followed by a steeper section in which the rate increases approximately linearly with sulphur dioxide concentration.

An attempt was made to deliniate areas of homogeneous and heterogeneous control by repeating runs under the same conditions, using one and two gram samples of the mineral. These results indicated that, in general for Series Al and A2, ie. low acid conditions, the rate appeared to be mainly homogeneously controlled at low sulphur dioxide concentrations. Series A3 appeared to be mainly heterogeneously controlled throughout.

The reproducibility of the results in these series was varied. Under some conditions the reproducibility was good-within 5%, but under other conditions variations of up to 30% were observed. In general the reproducibility was best in Series Al , the lowest acid series. The poor reproducibily in the other series was mainly evident at low concentrations of dissolved sulphur dioxide. The lack of reproducibility in these areas was thought to indicate that a complex kinetic situation was occurring.
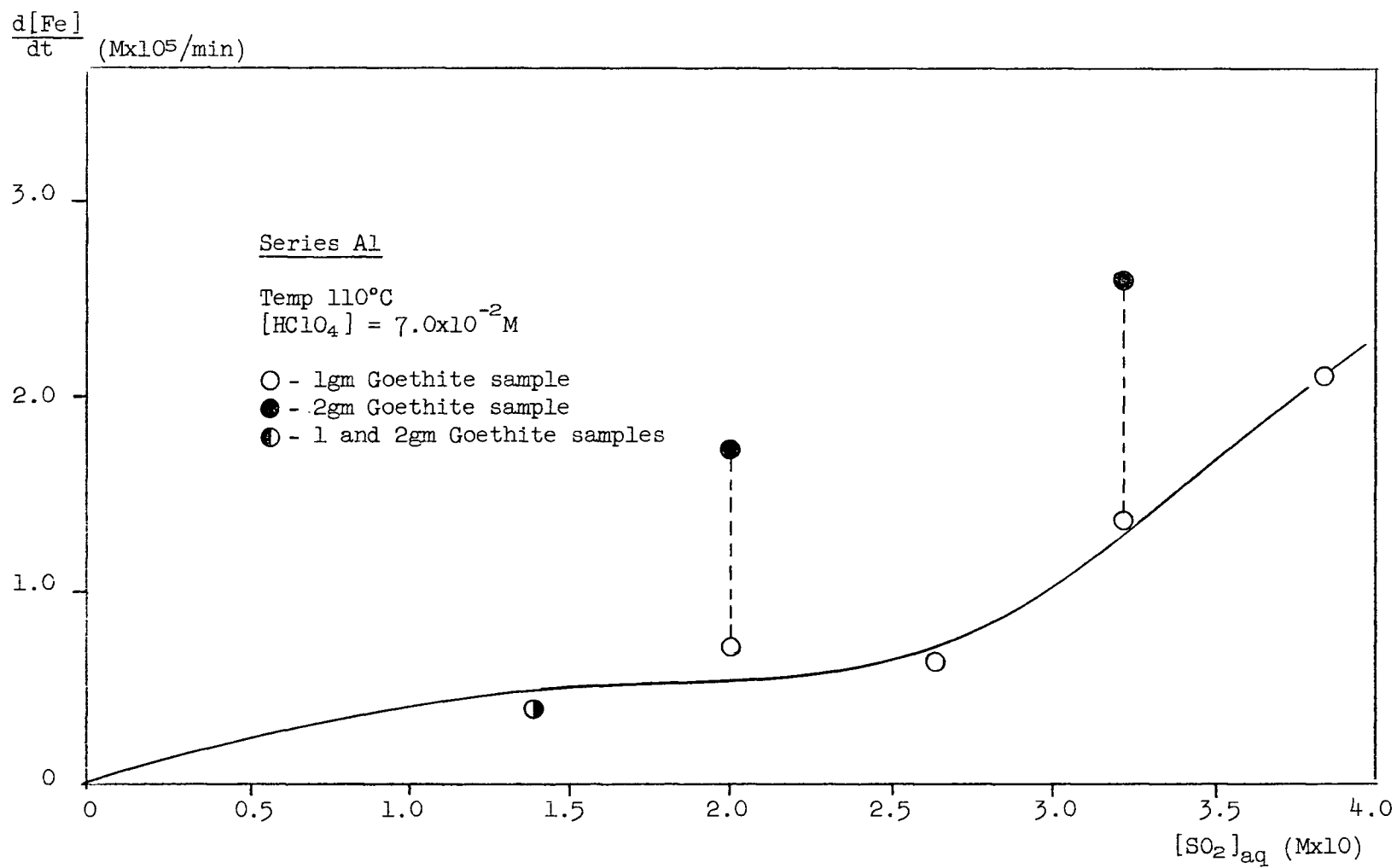
$\dfrac{d[Fe]}{dt}$ (Mx10⁵/min)

Series A1

Temp 110°C
$[HClO_4] = 7.0 \times 10^{-2} M$

◯ – 1gm Goethite sample
● – 2gm Goethite sample
◖ – 1 and 2gm Goethite samples

$[SO_2]_{aq}$ (Mx10)

Figure 9   Rate versus concentration of dissolved sulphur dioxide

$\frac{d[Fe]}{dt}$ (Mx10^5/min)

Series A2

Temp 110°C
$[HClO_4] = 1.4 \times 10^{-1}M$

○ - 1gm Goethite sample
● - 2gm Goethite sample
◑ - 1 and 2gm Goethite samples

1.5

1.0

0.5

0

0   0.5   1.0   1.5   2.0   2.5   3.0   3.5   4.0
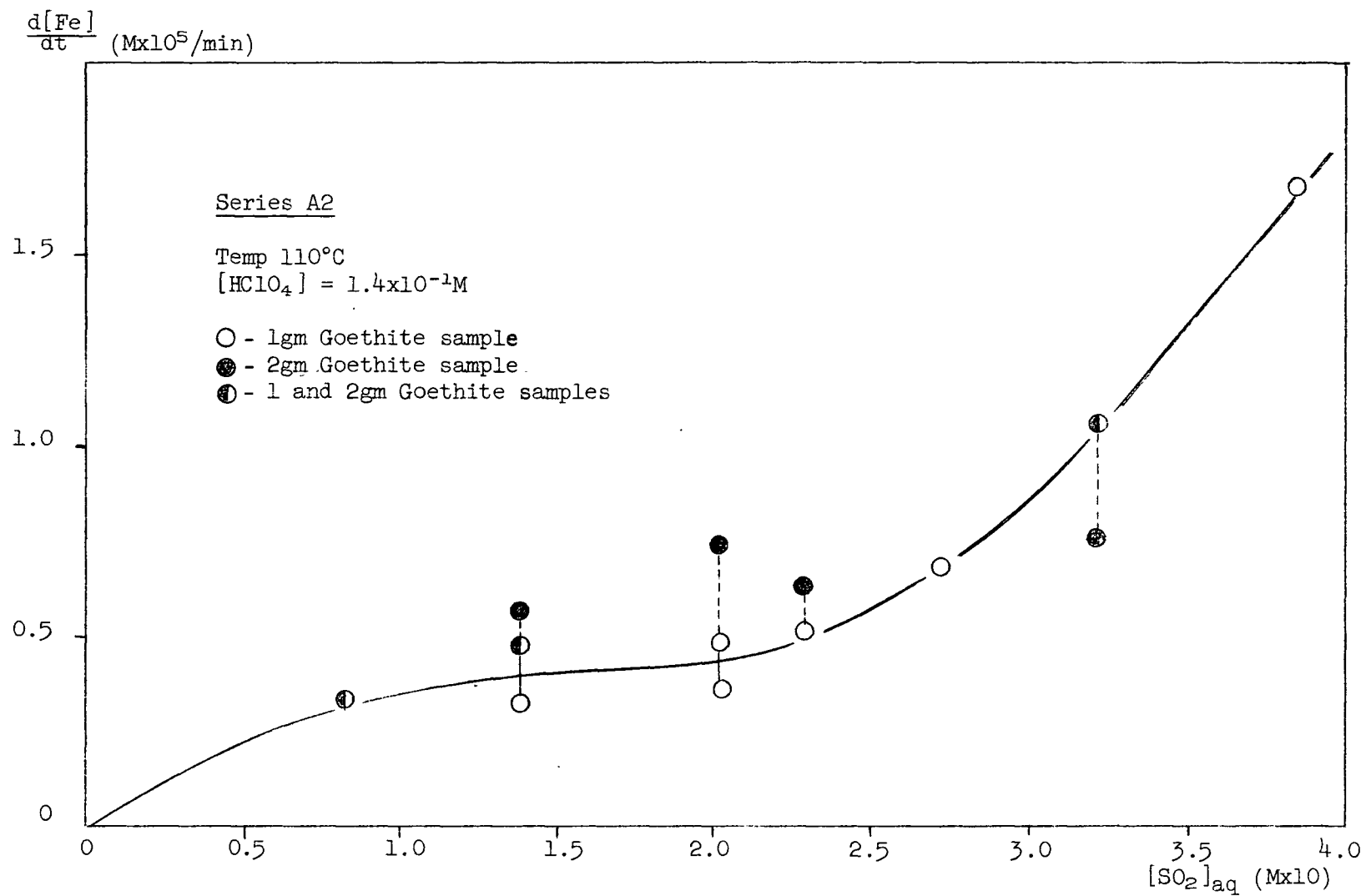
$[SO_2]_{aq}$ (Mx10)

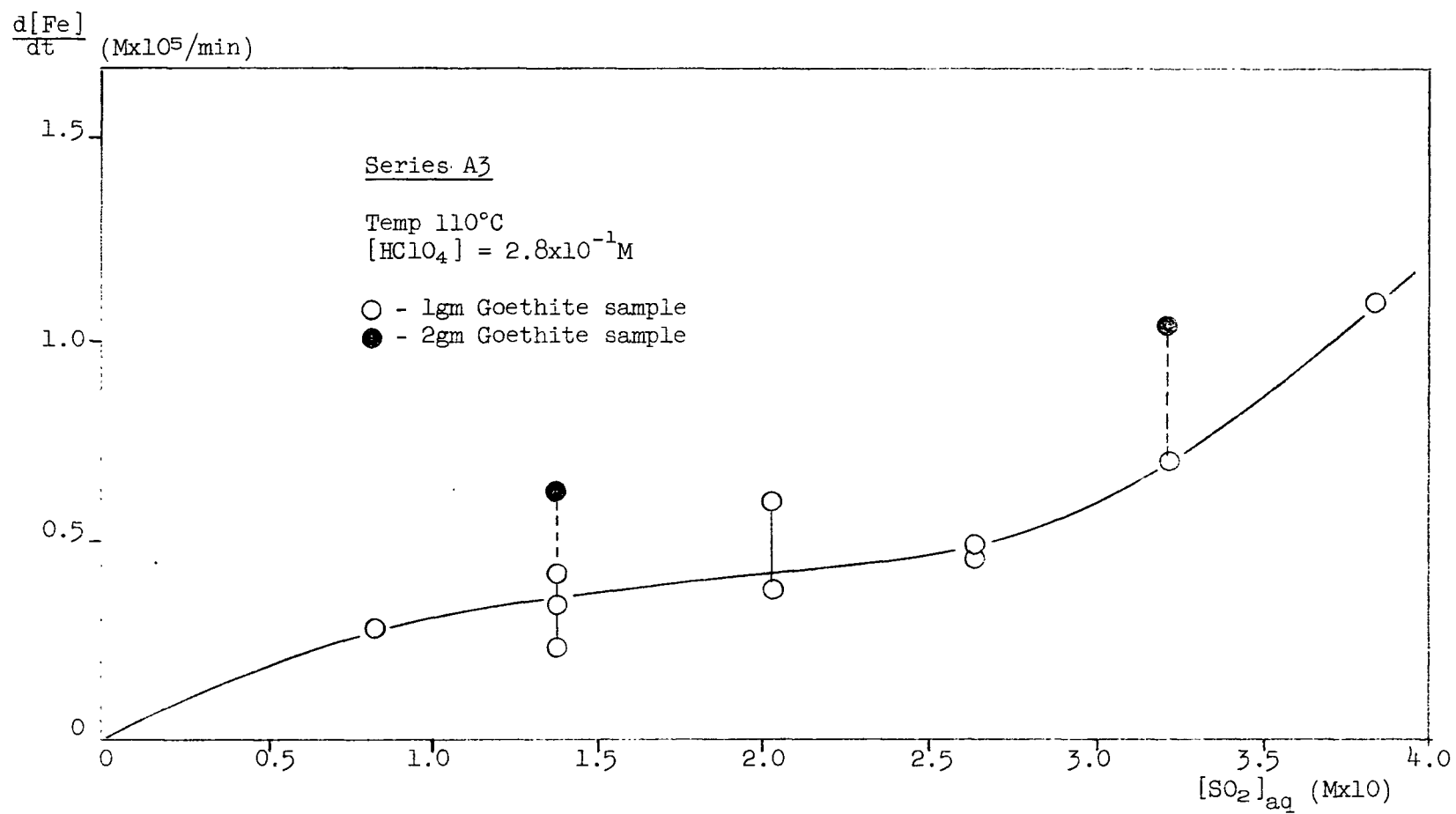Figure 10   Rate versus concentration of dissolved sulphur dioxide

Figure 11   Rate versus concentration of dissolved sulphur dioxide

The effect of varying acidity at constant sulphur dioxide concentration

A number of runs was carried out at different acidities at a constant low concentration of dissolved sulphur dioxide. These results are reported in Table IV (Appendix A). It may be seen that they confirm the observation that, at low concentrations of dissolved sulphur dioxide, the rate of dissolution is virtually independent of the acidity of the solution.

Sulphate analyses

In order to try to establish the stoichiometry of the reaction, the leach solutions of a number of runs were analysed for their sulphate content. In each case, the sample for sulphate analysis was taken 3 hours after the beginning of the run. The results are reported in Table V (Appendix A). The molar ratio of sulphate to iron was always greater than 1.5:1, the average value being 1.77:1

The effect of cupric ion on the system

Since copper is known to catalyse the homogeneous oxidation of sulphurous acid by ferric ion, several series of experiments were performed to determine the effect of cupric ion on the leaching of goethite with aqueous solutions of sulphur dioxide. Cupric ion was added as cupric perchlorate. The results are reported under the following headings:

i) Varying cupric ion concentration under conditions of constant acidity and constant sulphur dioxide concentration

ii)   Varying sulphur dioxide concentration at constant
acidity and constant inital cupric ion concentration

iii)   The effect of temperature on the cupric catalysed
reaction

iv)   The effect of cuprous ion in the absence of sulphur dioxide.

i)   Varying the cupric ion concentration at constant acidity and constant
sulphur dioxide concentration

Series B1 was carried out under conditions of low acidity and
low concentration of dissolved sulphur dioxide. The results of this
series may be found in Fig. 12, plotted as rate versus cupric ion con-
centration. Under these conditions in the absence of copper, the
reaction is homogeneously controlled. The rate is catalysed by the
addition of cupric ion to the system. At low concentrations of
cupric ion, the rate remains homogeneously controlled, but it becomes
heterogeneously controlled at higher cupric concentrations. This has
been illustrated in Fig. 12 by plotting results obtained using one and
two gram samples of goethite. It may be seen that as the rate becomes
fully heterogeneously controlled, the increase in rate slows down, but
then at higher cupric concentrations, the rate begins to increase
fairly rapidly again, still remaining heterogeneously controlled.

ii)   Varying the sulphur dioxide concentration at constant acidity and
constant initial cupric ion concentration

Series B2 was carried out to determine the effect of
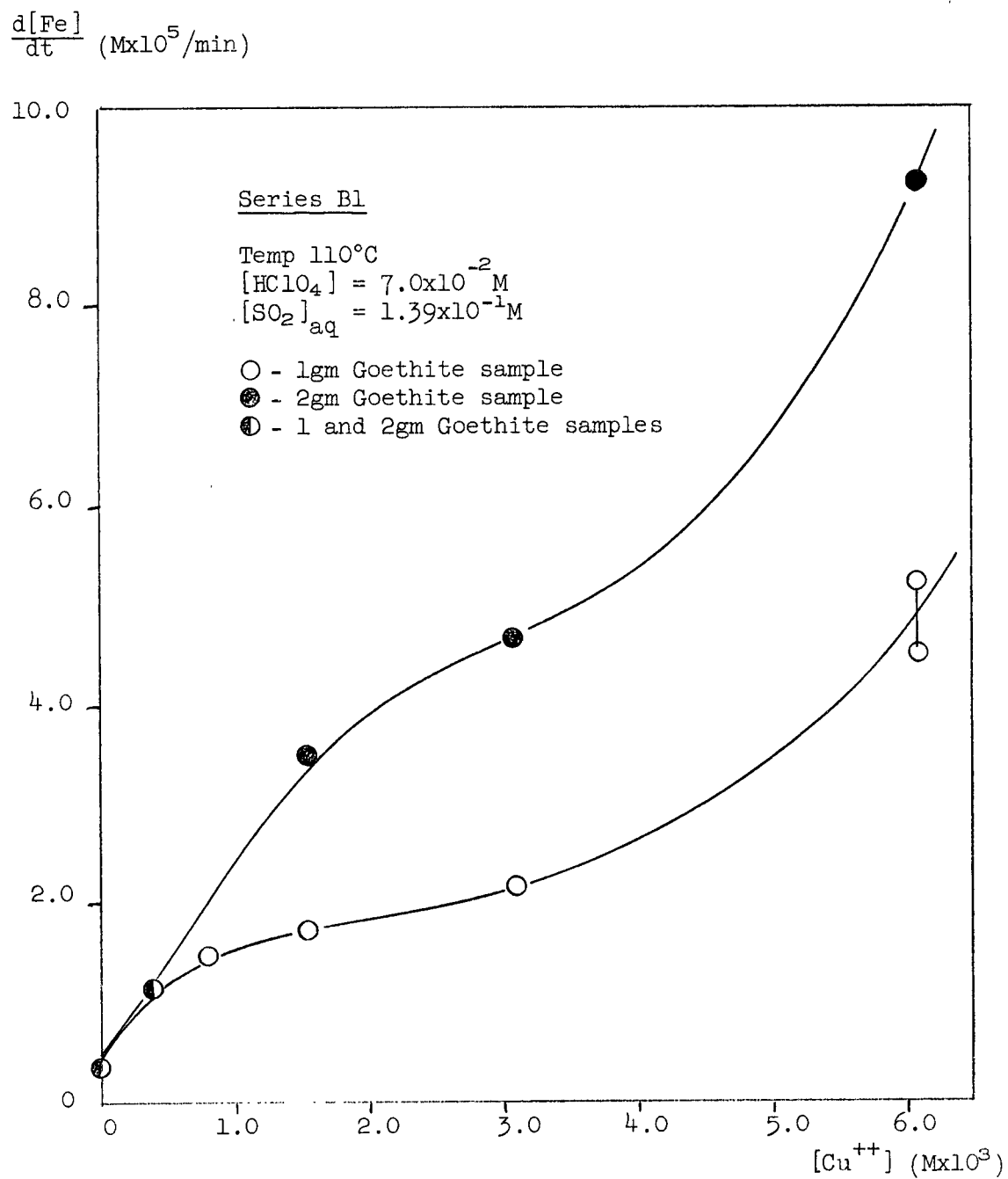
$\dfrac{d[Fe]}{dt}$ (Mx10^5/min)

Figure 12   Rate versus cupric ion concentration

increasing the concentration of dissolved sulphur dioxide under conditions of constant acidity and constant initial cupric ion concentration. The results may be found in Fig. 13 (Table VII Appendix A). It is evident that there is an optimum concentration of dissolved sulphur dioxide. At concentrations greater than the optimum, the rate begins to decrease.

An experiment was carried out to determine the amount of copper in solution at various sulphur dioxide concentrations. The initial reagent concentrations were the same as for Series B2. The solution was brought up to reaction temperature under a nitrogen atmosphere and a sample was taken. Sulphur dioxide was then introduced at a certain pressure. At the end of one hour, a further sample was taken and the sulphur dioxide pressure increased. This was repeated three times and the samples analysed for their copper content. The results are plotted in Fig. 14 (Table VIII Appendix A). It may be seen that the concentration of copper in solution decreases as soon as sulphur dioxide is introduced to the system. The copper concentration then remains constant until at higher sulphur dioxide concentrations, it begins to decrease again. This second decrease occurs at approximately the same sulphur dioxide concentration as the decrease in rate observed in Series B2. This is evident from a comparison of Figs. 13 and 14.

iii) The effect of temperature on the cupric catalysed reaction

In order to determine the activation energy of the cupric catalysed reaction, a series of experiments was performed in which the reaction temperature was varied, the reactant concentrations being kept
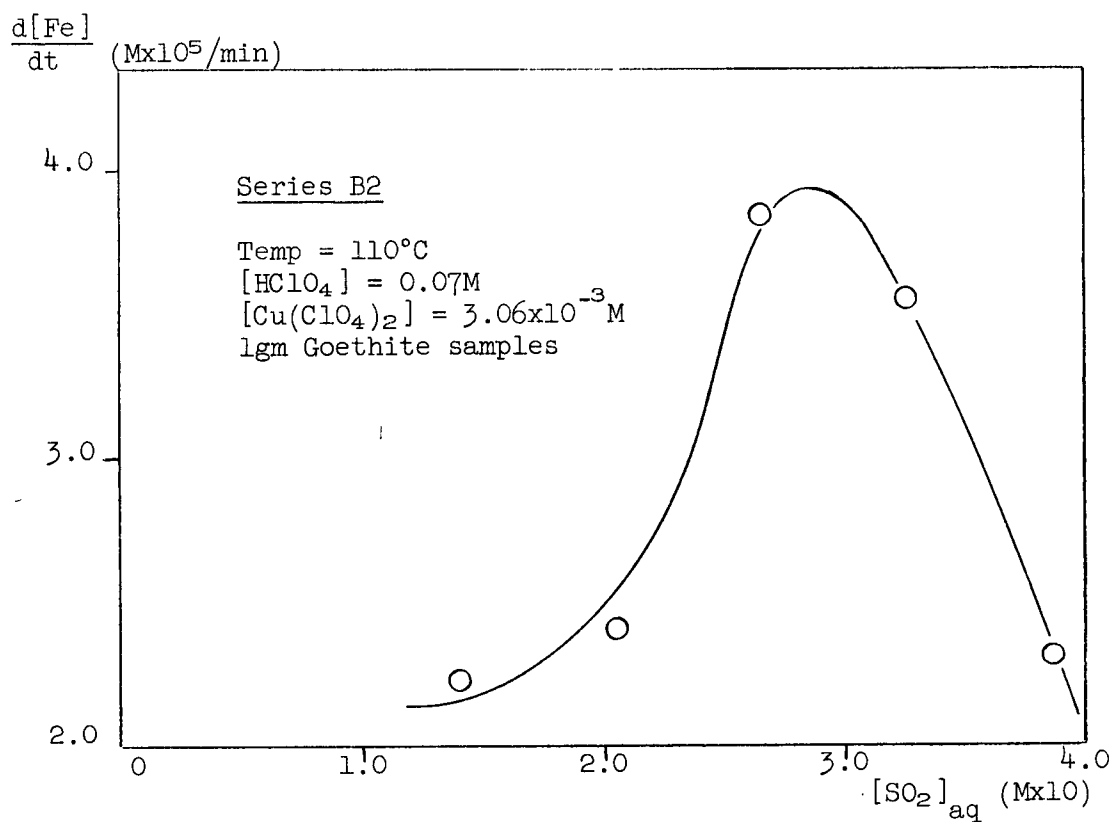
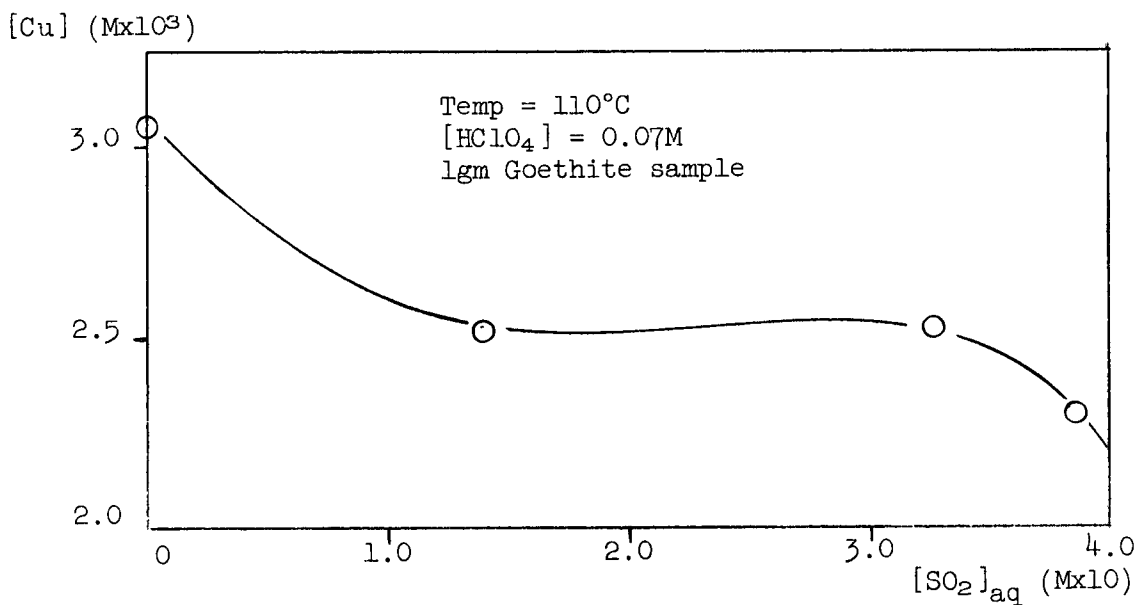Figure 13 Effect of increasing $[SO_2]_{aq}$ at constant initial cupric ion concentration

Figure 14 Effect of increasing $[SO_2]_{aq}$ on [Cu] in solution

constant. The concentration of dissolved sulphur dioxide was kept constant by varying the partial pressure of sulphur dioxide in accordance with the published solubility data of sulphur dioxide (See Appendix B). The results of this series are plotted on an Arrhenius diagram, Fig. 15 (Table IX Appendix A). The slope of this line corresponds to an activation energy of 23.1 KCal/mole.

iv) The effect of cuprous ion in the absence of sulphur dioxide

To determine whether cuprous ion could enter into the reaction, a run was carried out under conditions of high cupric ion concentration and low acidity. The reducing atmosphere was provided by introducing hydrogen into the system instead of sulphur dioxide. In this way, the effect of dissolved sulphur dioxide was eliminated, while still maintaining the reducing conditions necessary for the formation of some cuprous ion. The results of this run (Fig. 16), indicated that it is possible to dissolve iron from goethite in dilute perchloric acid solution in the presence of cuprous ion.
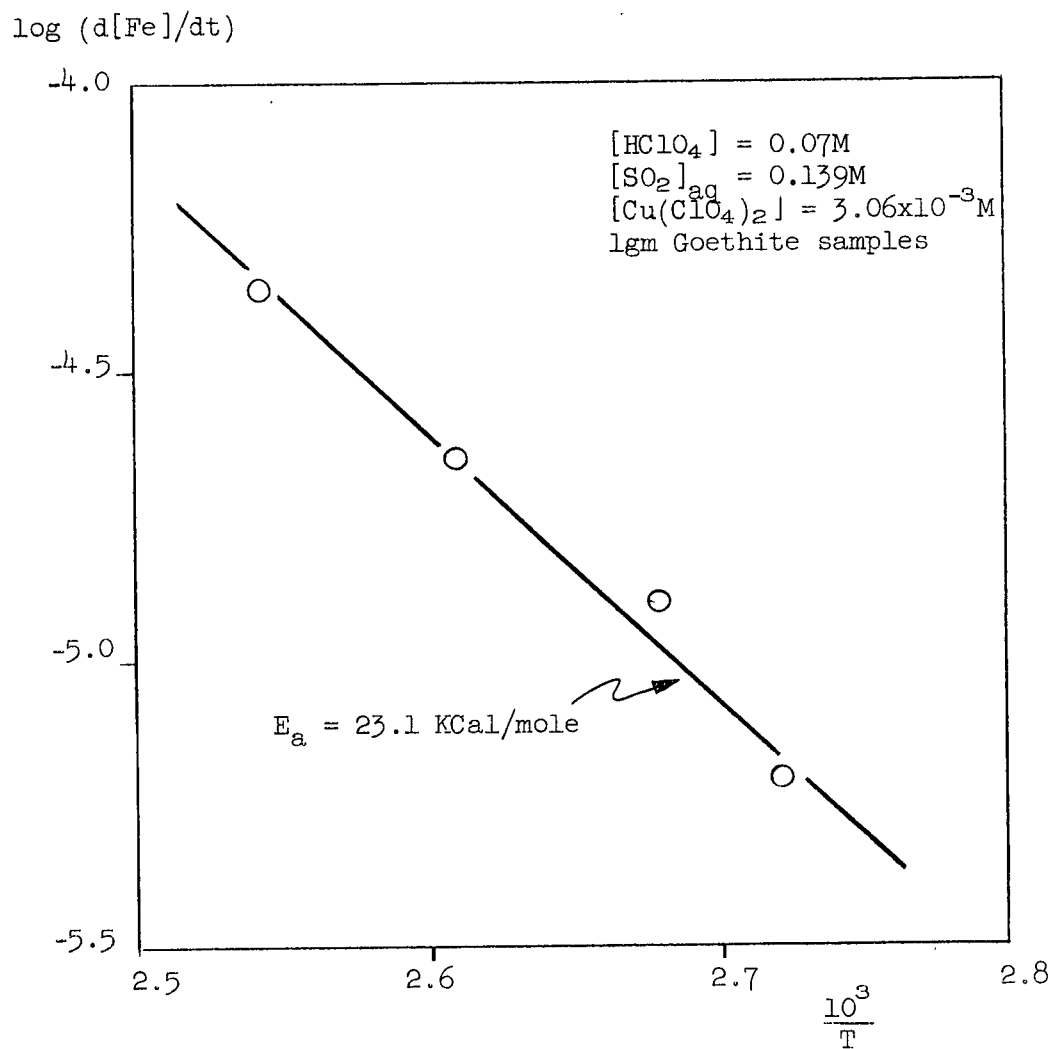
log (d[Fe]/dt)

$$[HClO_4] = 0.07M$$
$$[SO_2]_{aq} = 0.139M$$
$$[Cu(ClO_4)_2] = 3.06 \times 10^{-3}M$$
1gm Goethite samples

$$E_a = 23.1 \text{ KCal/mole}$$

$$\frac{10^3}{T}$$

Figure 15   Arrhenius plot for cupric catalysed dissolution

[Fe] Mx10^4

Temp = 110°C
[HClO$_4$] = 0.07M
H$_2$ p.p. = 90.0psig
[Cu(ClO$_4$)$_2$] = 6.10x10^{-3}M
1gm Goethite sample

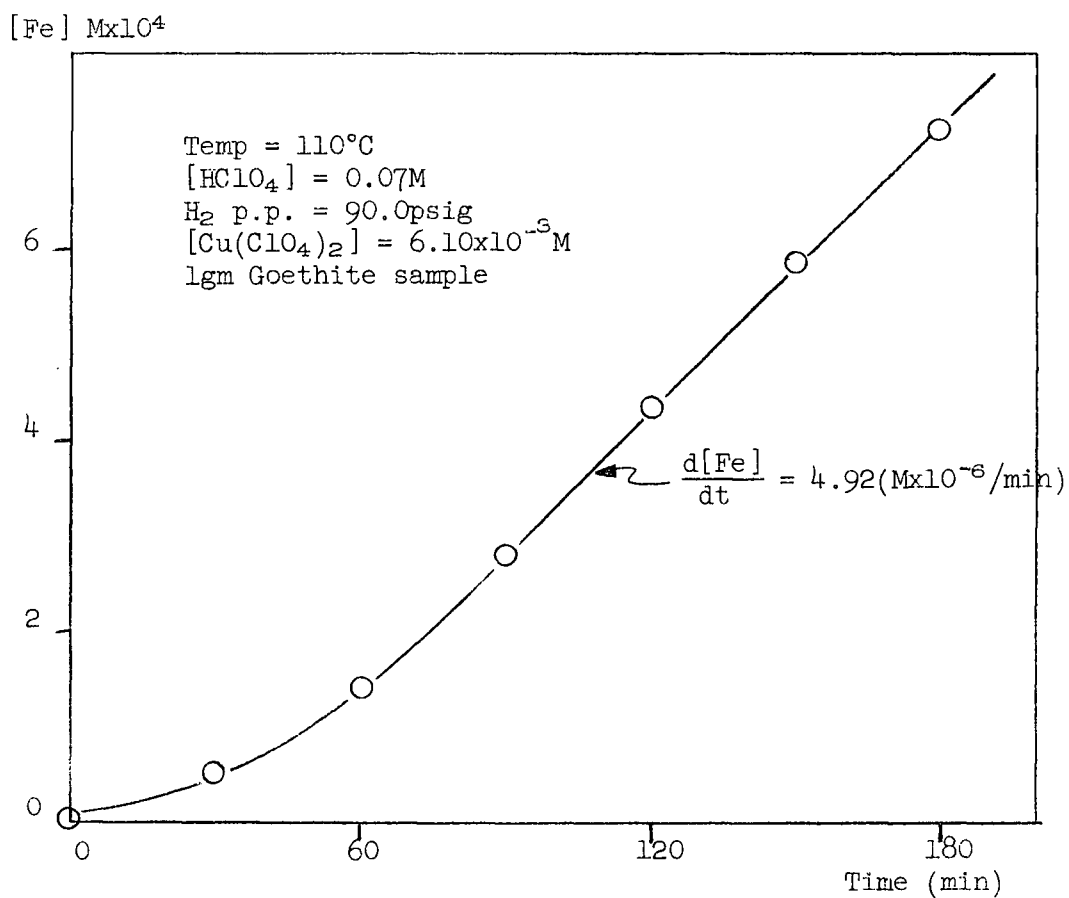$$\frac{d[Fe]}{dt} = 4.92(Mx10^{-6}/min)$$

Time (min)

Figure 16 Dissolution of goethite in dilute perchloric acid in the presence of copper under H$_2$ atmosphere

DISCUSSION

Direct Dissolution

The results of the direct dissolution experiments indicate
that:-

i) The rate of dissolution of goethite in sulphuric acid
increases approximately linearly with hydrogen ion activity over the range
of acid concentrations studied.

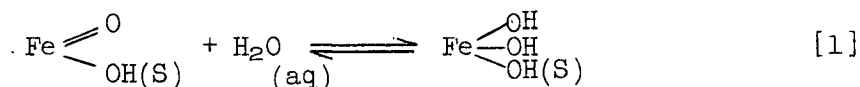ii) The activation energy for dissolution in sulphuric acid
is 18.2 KCal/mole.

iii) The rate of dissolution in sulphuric acid is faster than
in perchloric acid of the same molar concentration.

Similar results to these were reported by Azuma and
Kametani[46] for the dissolution of hematite, α-Fe$_2$O$_3$, in acid media
They showed that the activation energy of 20 ± 2 KCals/mole was virtually
independent of the type of acid used, that the rate of dissolution
increased with increasing hydrogen ion, and that the absolute rate of
dissolution depended upon the particular acid used. They demonstrated
that there was a direct relationship between the absolute rates of
dissolution and the stability constants for complexes formed by ferric
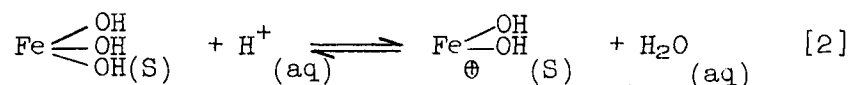ions with the anions of the various acids.

In the following discussion an attempt is made to relate the
results of this study and of Azuma and Kametani by postulating a general
mechanism which is operative during the direct dissolution of both
hydrated α-Fe$_2$O$_3$ (Goethite) and anhydrous α-Fe$_2$O$_3$ (Hematite) in acid
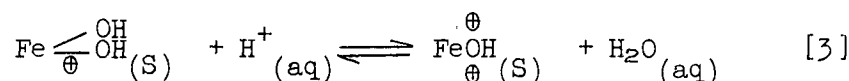
media.

It is considered that the first step in the dissolution of both hematite and goethite involves hydration of the oxide surface, so that they both take up similar surface configurations in aqueous solution designated in the following manner:

$$\text{Fe} \overset{O}{\underset{OH(S)}{\diagdown}} \; + \; H_2O_{(aq)} \; \rightleftharpoons \; \text{Fe} \overset{OH}{\underset{OH(S)}{\diagdown}} \underset{}{\overset{OH}{-}} \qquad [1]$$
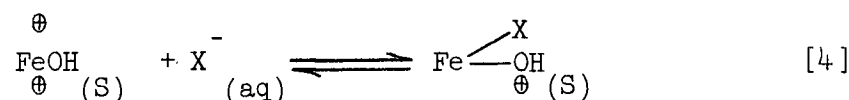
In this condition the oxide surface will probably have an overall negative charge due to the hydroxyl groups on the surface. In acid solution this is likely to rapidly undergo protonation:

$$\text{Fe} \overset{OH}{\underset{OH(S)}{\diagdown}} \underset{}{\overset{OH}{-}} \; + \; H^+_{(aq)} \; \rightleftharpoons \; \text{Fe} \overset{OH}{\underset{\oplus}{\diagdown}} \underset{(S)}{\overset{OH}{-}} \; + \; H_2O_{(aq)} \qquad [2]$$

This equilibrium, involving the first protonation of ferric hydroxide, has been reported to be the principal equilibrium occurring in solutions of pH 3 to 1 at $25°C$ [47]. At pH approaching 1 or less, a second protonation becomes increasingly likely-

$$\text{Fe} \overset{OH}{\underset{\oplus}{\diagdown}} \underset{(S)}{\overset{OH}{-}} \; + \; H^+_{(aq)} \; \rightleftharpoons \; \overset{\oplus}{\text{FeOH}}_{\underset{\oplus}{(S)}} \; + \; H_2O_{(aq)} \qquad [3]$$
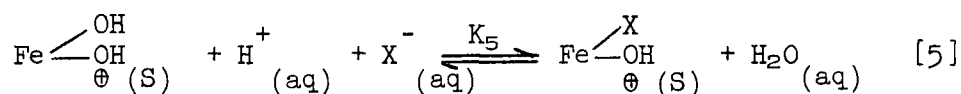
In order to account for the anion dependency shown on the rate of dissolution in various acids, it is suggested that anion adsorption takes place at the surface, following reation [3]

$$\overset{\oplus}{\underset{\oplus}{\text{FeOH}}}_{(S)} \; + \; X^-_{(aq)} \; \rightleftharpoons \; \text{Fe} \overset{X}{\underset{\oplus}{\diagdown}} \underset{(S)}{\overset{X}{-}} \qquad [4]$$

Assuming that, at any time, the concentration of $\overset{\oplus}{\underset{\oplus}{\text{FeOH}}}$ on

the surface is small, ie. reaction [4] takes place rapidly following

reaction [3], then an overall equilibrium may be written-

$$Fe\diagdown\substack{OH \\ OH \\ \oplus}(S) \; + \; H^+_{(aq)} \; + \; X^-_{(aq)} \; \underset{}{\overset{K_5}{\rightleftharpoons}} \; Fe\diagdown\substack{X \\ OH \\ \oplus}(S) \; + \; H_2O_{(aq)} \qquad [5]$$

Reaction [5] is, in effect, an anion exchange, resulting in

the exchange of a hydroxyl ion for an anion, X^-, at the oxide surface.

Ferric hydroxide has been shown to have an anion exchange capacity in

· acid solution[48].

Two different mechanisms leading to the dissolution of

ferric ion are possible following reaction [5].

Mechanism (a) Reaction [5] is followed directly by a rate-controlling

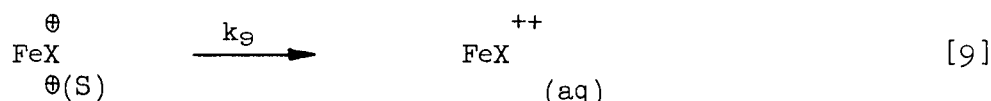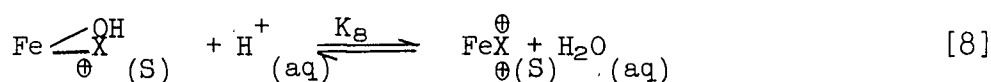desorption of the hydroxy-ferric complex:

$$Fe\diagdown\substack{X \\ OH \\ \oplus}(S) \; \xrightarrow{k_6} \; Fe \; X \; OH^+_{(aq)} \qquad [6]$$
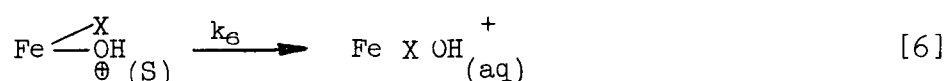
·The rate equation for this mechanism may be written as:

$$\frac{d \, (FeXOH^+)}{dt} = k_6 K_5 [Fe\diagdown\substack{OH \\ OH \\ \oplus}] \, [X^-] \, [H^+] \qquad [7]$$

If it is assumed that the whole oxide surface undergoes the

first protonation (reaction [2]), then $[Fe\diagdown\substack{OH \\ OH \\ \oplus}]$ should be a constant,

and may be regarded as the total number of sites. According to this

mechanism, the rate of dissolution will depend on both the concentration

of hydrogen ion, and the concentration of anion in solution. ·Differences

in absolute rates of dissolution in different acids may be accounted

for by variations in K_5. The value of K_5 should be related to the

complexing affinity of the anion, X^-, for ferric ion, since Azuma and Kametani have shown that there is a direct relationship between the rate of dissolution and the stability constant of the ferric-anion complex.

Mechanism (b)   The assumption that K_5 varies for different anions may be incorrect and that in fact, K_5 may be large for all anions, so that reaction [5] lies well to the right. If this is the case, it is suggested that dissolution may proceed via another protonation of the sites containing an adsorbed anion:

$$Fe \overset{OH}{\underset{\oplus}{\diagdown X}}_{(S)} + H^+_{(aq)} \underset{}{\overset{K_8}{\rightleftharpoons}} \overset{\oplus}{FeX}_{\oplus(S)} + H_2O_{(aq)} \tag{8}$$

$$\overset{\oplus}{FeX}_{\oplus(S)} \xrightarrow{k_9} \overset{++}{FeX}_{(aq)} \tag{9}$$

In this case, the rate equation is:

$$\frac{d(\overset{++}{FeX})}{dt} = k_9 K_8 [Fe \overset{OH}{\underset{\oplus}{\diagdown OH}}] \cdot [H^+] \tag{10}$$

Dissolution occurring via this mechanism should depend on the concentration of hydrogen ion in solution, but should be independent of the concentration of anion. Differences in the absolute rate of dissolution for different anions would be due to different values of K_8.

The experimental evidence is not considered sufficient at present to favour either one of these mechanisms (a) or (b). Fig. 3 shows that over the range of concentrations studied, the dissolution of iron from goethite in sulphuric acid solution follows an approximately linear dependence on the activity of hydrogen ion. This might suggest that

mechanism (b) was operative. However mechanism (a) could also show a linear dependence on hydrogen ion if $[X^-]$ remained constant with increasing acid concentration (See equation [7]). This would be the case if sulphate, rather than bisulphate, was the adsorbing anion in sulphuric acid solutions, since the second dissociation constant of sulphuric acid is small compared with the first.

Further studies are necessary to enable a distinction to be made between these two mechanisms. The addition of anion at a fairly high acid strength should give a good indication as to which mechanism is operative, since dissolution occurring via mechanism (a) should be dependent on the anion concentration whereas via mechanism (b) it should be independent of anion concentration.

The postulation that the rate controlling step is the desorption of a complex species from the oxide surface is made since the activation energy for the process has been shown to be similar for different acids, indicating a similar rate controlling step in each case. The reported value of 20 ± 2 KCal/mole for hematite and the value determined in this study of 18.2 KCal/mole for goethite are considered to be in good agreement. The values of these activation energies are high enough to indicate that a chemical desorption is taking place, rather than a diffusion process. The spread in values between different acids, ie. ± 2 KCal/mole is thought to be sufficient to account for the observed differences in rates in different acids. The change in absolute rate has been postulated to be either a function of the pre-equilibrium anion exchange reaction (reaction [5]), or the pre-equilibrium proton attack (reaction [8]). The enthalpy involved in these pre-equilibrium reactions will

be a part of the measured activation energies. Changes in this enthalpy due to involvement of different anions in these equilibria could account for the observed spread in the activation energies.

This argument may be demonstrated semi-quantitatively as follows-

The rate of dissolution via either mechanism (a) or (b) may be expressed in terms of the activation energy by the Arrhenius equation:

$$Rate = Ae^{-\frac{E_d + \Delta H}{RT}}$$

where   A = the Arrhenius constant

E_d = the activation energy of the desorption step

ΔH = the enthalpy of the pre-equilibrium reaction

The measured activation energy will consist of the sum of E_d and ΔH. It has been shown that at 130°C, the rate of dissolution in sulphuric acid is of the order of 35 times faster than in perchloric acid at similiar molar concentrations.

Thus: $$\frac{Rate_{H_2SO_4}}{Rate_{HClO_4}} = \frac{Ae^{-\frac{E_d + \Delta H_1}{RT}}}{Ae^{-\frac{E_d + \Delta H_2}{RT}}} = 35$$

where ΔH_1 and ΔH_2 are the enthalpies associated with the pre-equilibria involving H_2SO_4 and $HClO_4$ respectively. If it is assumed that E_d is virtually independent of the particular desorbing species, then:

$$\frac{-\Delta H_1}{2.303RT} + \frac{\Delta H_2}{2.303RT} = \log 35$$

$$\therefore \quad \Delta H_2 - \Delta H_1 = 2.303RT \log 35$$

$$= 4.575(403)(1.544)$$

$$= \underline{2.85 \text{ KCal}}$$

Thus the difference between the enthalpies associated with the pre-equilibria involving these two acids is less than the reported spread of 4 KCals in the measured activation energies for dissolution in various acids.

Reductive Dissolution

Solutions of sulphur dioxide in water have traditionally been referred to as sulphurous acid solutions. Although the anions of this acid, bisulphite (HSO_3^-) and sulphite ($SO_3^=$), have been identified in solution, undissociated sulphurous acid has not (See Appendix B). It is believed that the bulk of the sulphur dioxide in solution exists as neutral molecules with an associated hydration sheath of water molecules. However, for the purposes of this discussion, the term sulphurous acid, and its traditionally accepted formula H_2SO_3, will be used, instead of the more correct term, hydrated sulphur dioxide (SO_2xH_2O).

It is considered that the reductive dissolution of goethite in sulphurous acid, as in the case of direct dissolution, involves hydration of the oxide surface as a prerequisite to further reaction-

$$Fe\overset{O}{\underset{OH}{\lessgtr}} + H_2O \rightleftharpoons Fe\overset{OH}{\underset{OH}{\lessgtr}}OH \qquad [1]$$
$$(S) \qquad (aq) \qquad\qquad (S)$$
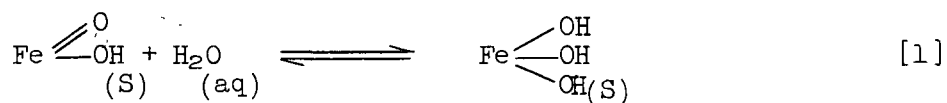
The effect of acidity and dissolved sulphur dioxide concentration

The results for Series Al, A2, and A3, in which the partial pressure of sulphur dioxide was varied at three different acidities, are plotted on the same diagram against the concentration of dissolved sulphur dioxide-See Fig. 17. It may be seen that at low concentrations of dissolved sulphur dioxide the rate increases slowly, and is virtually independent of acidity. At higher sulphur dioxide concentrations, the rate begins to increase more rapidly in an approximately linear fashion, and a marked dependency on acidity becomes evident.

$\dfrac{d[Fe]}{dt}$ (Mx10^5/min)

Temp = 110°C
1gm Goethite samples

O - [HClO$_4$] = 0.07M
● - [HClO$_4$] = 0.14M
⊗ - [HClO$_4$] = 0.28M

2.0

1.5

1.0

0.5

0

0   1.0   2.0   3.0   4.0
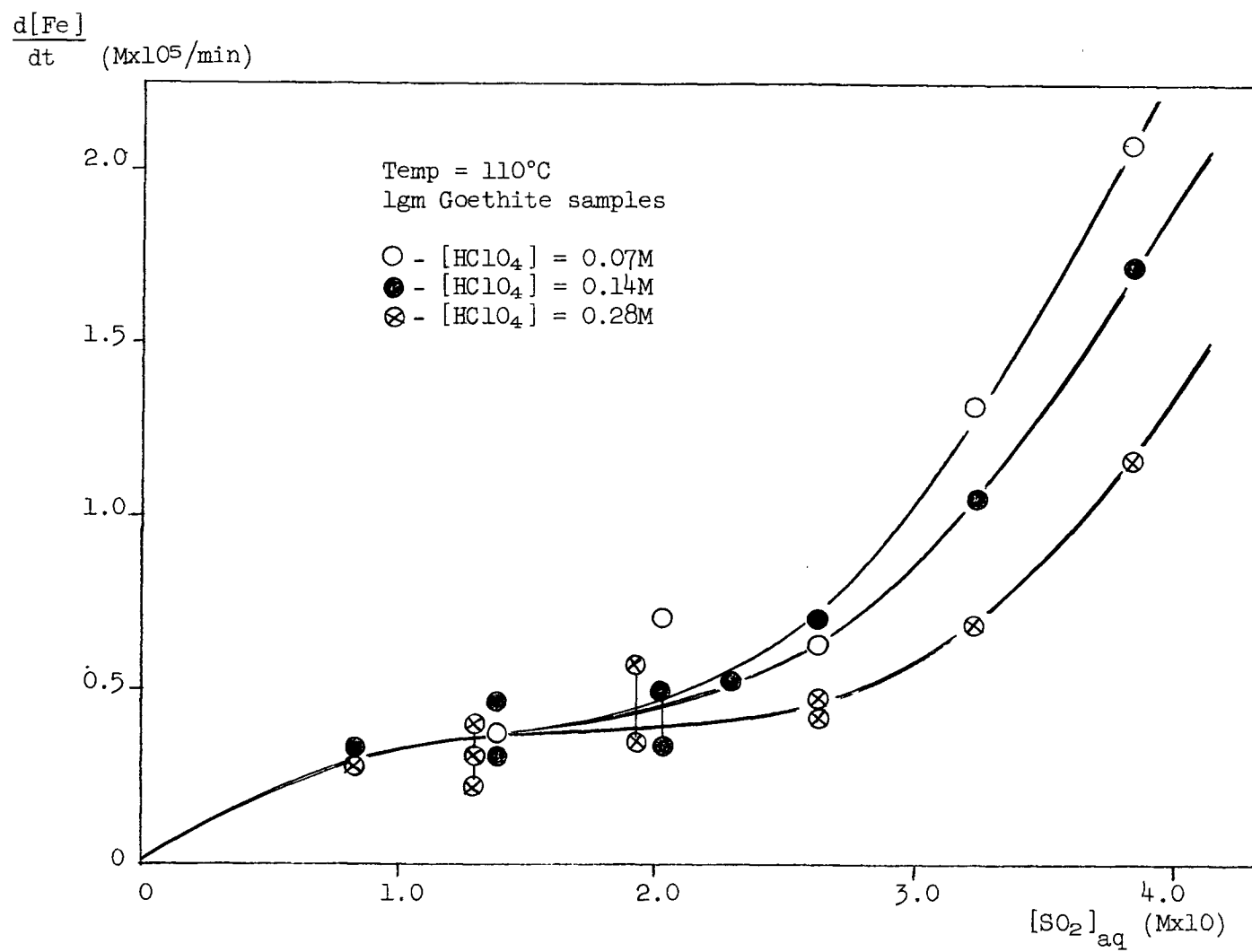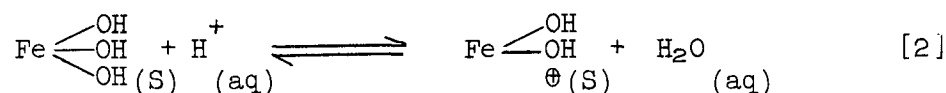
[SO$_2$]$_{aq}$ (Mx10)

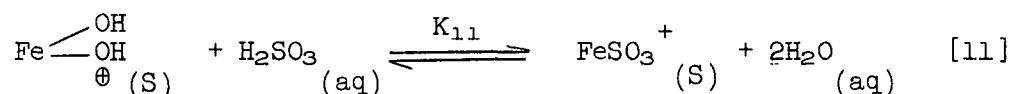Figure 17   Rate versus concentration of dissolved sulphur dioxide at various acidities
(Series A1, A2, and A3)

The range of hydrogen ion concentration in which these series of runs were carried out was $7 \times 10^{-2}M$ to $2.8 \times 10^{-1}M$. Under these conditions, protonation of the surface, similar to that postulated for direct dissolution, is thought to occur-

$$Fe \overset{OH}{\underset{OH}{\overset{|}{\underset{|}{-}}}} OH\ (S) + H^+_{(aq)} \rightleftharpoons Fe \overset{OH}{\underset{\oplus (S)}{\overset{|}{-}}} OH + H_2O_{(aq)} \qquad [2]$$

At 110°C, the apparent dissociation constant of sulphurous acid has been calculated to be $Ka = 1.37 \times 10^{-3}$ (See Appendix B). The low value of this constant indicates that the majority of the dissolved sulphur dioxide will remain undissociated in solution, and it is thought likely that neutral sulphurous acid molecules are the reacting species at the oxide surface.

Furthermore, in order to account for the observed hydrogen ion dependency at higher concentrations of dissolved sulphur dioxide, it is postulated that the sulphurous acid can react at the oxide surface via two distinct mechanisms, (a) and (b) -

Mechanism (a) Reaction involving the removal of two hydroxyl groups from the surface, and resulting in the formation of a ferric sulphite complex on the surface-
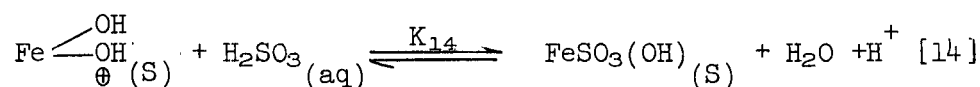
$$Fe \overset{OH}{\underset{\oplus \ (S)}{\overset{|}{-}}} OH + H_2SO_{3\ (aq)} \overset{K_{11}}{\rightleftharpoons} FeSO_3^+{}_{(S)} + 2H_2O_{(aq)} \qquad [11]$$

The next, and rate-controlling step, is considered to be the desorption of this complex from the surface into solution-

$$FeSO_3^+{}_{(S)} \overset{k_{12}}{\longrightarrow} FeSO_3^+{}_{(aq)} \qquad [12]$$
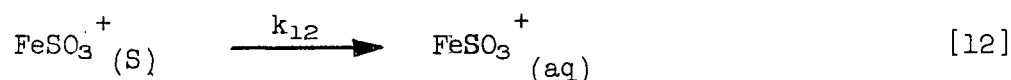
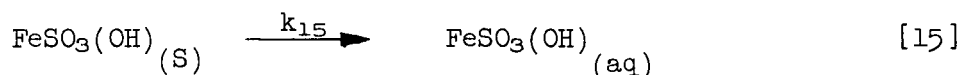The rate equation for these two steps, assuming Reaction[11] is in equilibrium, may be written as:

$$\frac{d\ Fe(SO_3)^+}{dt} = k_{12}K_{11}\ [Fe{\overset{OH}{\underset{\oplus}{\diagup}}\!\!-OH}]\ [H_2SO_3] \qquad [13]$$

Mechanism (b)   Reaction involving the removal of one hydroxyl group from the oxide surface, resulting in the formation of a hydroxyl-ferric sulphite complex

$$Fe{\overset{OH}{\underset{\oplus}{\diagup}}\!\!-OH}_{(S)} + H_2SO_3\ _{(aq)} \overset{K_{14}}{\rightleftharpoons} FeSO_3(OH)_{(S)} + H_2O + H^+ \qquad [14]$$

Again, the rate controlling step is considered to be desorption of the complex from the surface into solution-

$$FeSO_3(OH)_{(S)} \xrightarrow{k_{15}} FeSO_3(OH)_{(aq)} \qquad [15]$$

Assuming Reaction [14] is in equilibrium, the rate equation for the dissolution of iron via this mechanism may be written as-

$$\frac{d\ (FeSO_3(OH))}{dt} = \frac{k_{15}K_{14}\ [Fe{\overset{OH}{\underset{\oplus}{\diagup}}\!\!-OH}]\ [H_2SO_3]}{[H^+]} \qquad [16]$$

If both of these mechanisms (a) and (b), contribute to the dissolution of iron from goethite in sulphurous acid, their rate equations may be combined to give an overall rate equation-

$$\frac{d\ (Fe)}{dt} = k_{12}K_1[Fe{\overset{OH}{\underset{\oplus}{\diagup}}\!\!-OH}]\ [H_2SO_3] + \frac{k_{15}K_{14}\ [Fe{\overset{OH}{\underset{\oplus}{\diagup}}\!\!-OH}]\ [H_2SO_3]}{[H^+]} \qquad [17]$$

If it is assumed that the number of sites, ie. [Fe${\overset{OH}{\underset{\oplus}{\diagup}}\!\!-OH}$],

remains constant for a given surface area of mineral, then it may be seen that the rate of dissolution of iron is a function of two terms, both directly proportional to the concentration of sulphurous acid. However one term is independent of, and the other inversely proportional to, the concentration of hydrogen ion.

The results show that the rate is virtually independent of hydrogen ion concentration at low concentrations of dissolved sulphur dioxide, suggesting that mechanism (a) is predominant. As the sulphur dioxide concentration is increased, an inverse dependency of rate on hydrogen ion concentration becomes evident, indicating that mechanism (b) becomes increasingly predominant. The observed hydrogen ion dependency is less than $\frac{1}{[H^+]}$. This observation agrees with the above rate equation, since it is comprised of two terms, one of which is independent of hydrogen ion concentration. Thus the overall rate should show a dependency on hydrogen ion concentration which lies between the limits set by these two terms.

The mechanisms outlined above can be used to show why homogeneous control of the reaction is observed under certain conditions. Homogeneous control is generally evident at low concentrations of dissolved sulphur dioxide. Under these conditions, it has been suggested that mechanism (a) is predominant, and that the rate controlling step is the desorption of the cationic ferric sulphite complex. For the reaction to become homogeneously controlled, the rate controlling heterogeneous step must reach an equilibrium. This means that readsorption of the cationic ferric sulphite complex would have to be rapid compared with its rate of

desorption.

Since hydrated iron oxide is known to have anion exchange properties under acid conditions, it is unlikely that a cationic complex could be rapidly readsorbed back on to the oxide surface. It is thought to be more likely that after desorption, the ferric sulphite complex reacts with bisulphite ion to form an anionic ferric sulphite complex, possibly:-

$$FeSO_3^+ + HSO_3^- \longrightarrow Fe(SO_3)_2^- + H^+ \qquad [18]$$
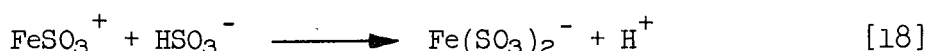
It is suggested that $Fe(SO_3)_2^-$ is the species that can adsorb back rapidly on to the oxide surface and create an equilibrium situation, so that a homogeneous reaction then becomes rate controlling.

The possible sequences of reactions in solution are numerous. However each sequence should result in the same oxidation products, namely sulphate and dithionate[11], but proportions of these species formed will probably depend on the mechanism involved. The mechanism which will predominate depends mainly on which ferric-sulphur IV species are stable under the particular conditions. As was pointed out in the literature review section, two series of ferric-sulphur IV complexes are possible - those involving sulphite ions and having the general formula $Fe(SO_3)_n^{3-2n}$, and those involving bisulphite ions, the general formula being $Fe(HSO_3)_n^{3-n}$. Until information is available on the stability of these complexes under various conditions, statements made concerning homogeneous reactions in this system must be purely speculative.

However, since it has been suggested that the anionic ferric disulphite complex, $Fe(SO_3)_2^-$, is predominant under conditions of low sulphur dioxide concentrations, a mechanism will be postulated involving this complex. Even if this assumption is incorrect, the general principles involved should apply to mechanisms involving other complexes.

The first step in the reduction of ferric iron is thought to involve the collision of two ferric disulphite complexes. This is in agreement with the work of Bassett and Parker[10]. Depending on the movement of electrons between the two complexes, either sulphate or dithionate could be formed as oxidation products. The reaction involving sulphate production may be written as-

$$2Fe(SO_3)_2^- \longrightarrow 2Fe^{++} + SO_3 + 3SO_3^= \qquad [19]$$
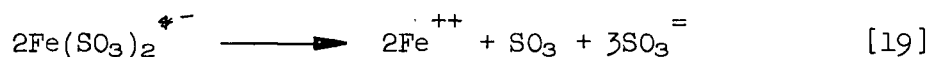
Sulphur trioxide would react immediately with water to form sulphate
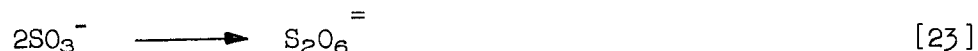
$$SO_3 + H_2O \longrightarrow SO_4^= + 2H^+ \qquad [20]$$
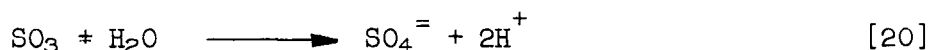
Under acid conditions, free sulphite ions would be very unstable and probably react with protons to form bisulphite

$$3SO_3^= + 3H^+ \longrightarrow 3HSO_3^- \qquad [21]$$

The production of dithionate involves the discharge of two singly charged sulphite free radicals-

$$2Fe(SO_3)_2^- \longrightarrow 2Fe^{2+} + 2SO_3^= + 2SO_3^{\dot=} \qquad [22]$$
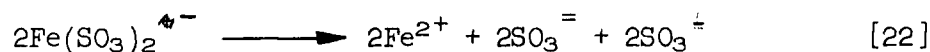
Dithionate can then result from dimerisation of these free radicals-

$$2SO_3^- \longrightarrow S_2O_6^=$$ [23]

As before, the sulphite ions would probably react to form bisulphite

$$2SO_3^= + 2H^+ \longrightarrow 2HSO_3^-$$ [24]

In order to try to establish the stoichiometry of the reactions, sulphate determinations were carried out on the final leach solutions obtained at the end of a number of runs. The sulphate to iron molar ratios that were determined were all greater than 1.5 to 1 (See Table V Appendix A). If sulphate production occurs via reactions [19] and [20] then the maximum sulphate to iron molar ratio would be 0.5 to 1. This must be the maximum ratio that can occur in this system since the formation of sulphate from the anionic species of sulphurous acid involves the discharge of two electrons. These can only be discharged on to two ferric ions to form ferrous ions, resulting in a sulphate to iron ratio of 0.5: 1.

The reasons for the relatively high concentrations of sulphate determined in this study are not known, but it is thought that it may be due to oxidation of sulphurous acid by perchloric acid. It is also possible that traces of chloric acid, which is a strong oxidising agent, were present in the perchloric acid. Oxidation by residual dissolved
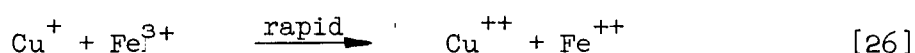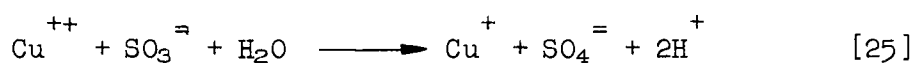
oxygen in the water is thought to be unlikely, since the solution was always boiled under a nitrogen atmosphere, before introduction of the sulphur dioxide.

The effect of cupric ion

The majority of the runs in which copper was added to the system were carried out under conditions of low acidity and low dissolved sulphur dioxide concentration-conditons under which mechanism (a) is postulated to be the dominant dissolution mechanism. Under these conditions, the rate was found to be homogeneously controlled in the absence of copper.

It was found that additions of cupric ion to the system could catalyse the rate of dissolution. It may be seen from Fig. 12 that, at low cupric ion concentrations, the rate remains homogeneously controlled, but that at higher concentrations, the control becomes heterogeneous.

The reactions of cupric ion in the ferric iron-sulphurous acid system have been postulated to be[11] -

$$Cu^{++} + SO_3^{=} + H_2O \longrightarrow Cu^{+} + SO_4^{=} + 2H^{+} \qquad [25]$$
$$Cu^{+} + Fe^{3+} \xrightarrow{\text{rapid}} Cu^{++} + Fe^{++} \qquad [26]$$

Under the conditions of this study, the concentration of free ferric ion in solution is likely to be very low. It is thought more likely that cuprous ion formed by Reaction [25] will react rapidly with the cationic ferric sulphite complex as it desorbs from the

oxide surface:-

$$FeSO_3^+ + Cu^+ \xrightarrow{\text{rapid}} FeSO_3 + Cu^{++} \qquad [27]$$
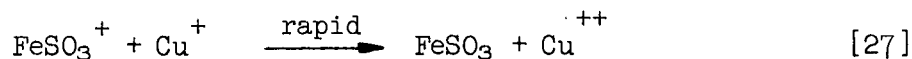
Ferrous sulphite, which is a neutral molecule, should not have the same tedency to readsorb back on to the oxide as does anionic ferric disulphite formed by Reaction [18]. It is more likely that ferrous sulphite would react with a proton and form ferrous ion and bisulphite ion. It is considered that the results illustrated in Fig. 12 can be explained by postulating competition between Reactions [18] and [27]. As the concentration of cupric ion in solution is increased, Reaction [27] becomes increasingly predominant. The rate can speed up due to depletion of the "insoluble" ferric disulphite complex, until the rate of desorption of the ferric sulphite complex becomes rate controlling (Reaction [12]). An activation energy measurement was carried out under conditions where fully heterogeneous control was observed in the presence of cupric ion (Fig. 15). The determined value of 23.1 KCals/mole is thought to be in good agreement with the reported value of 20 ± 2 KCal/mole for the direct dissolution of hematite in acid media. Under these conditions, it has already been postulated that the rate controlling step is the desorption of cationic species from the oxide surface.

The upward trend in the rate with increasing cupric ion, after heterogeneous control has been achieved is not understood (See Fig. 12). It is suggested that cuprous ion may be able to react at the surface of the oxide and reduce ferric iron to the ferrous state. At sufficiently high copper concentrations, there may be enough cuprous ion formed to cause appreciable dissolution via this mechanism. Some

support for this argument is provided by the experiment performed in which the reducing conditions were created by a hydrogen atmosphere instead of sulphur dioxide (See Fig. 16). Under these conditions, the observed dissolution must involve reactions with copper, presumably as cuprous ion at the oxide surface. Further study on this system is required.

The effect of increasing the concentration of dissolved sulphur dioxide under conditions of constant acidity and constant cupric ion concentration (Series B2) is shown in Fig. 13. The decrease in the rate at high concentrations of dissolved sulphur dioxide is considered to be due to the conditions becoming sufficiently reducing to precipitate copper metal from solution. In this way, the catalytic effect of cupric ion would be reduced due to a decrease in its concentration. Qualitative support for this argument is shown in Fig. 14. The concentration of copper in solution was measured at various concentrations of dissolved sulphur dioxide. A comparison of Figs. 13 and 14 shows that the concentration of copper in solution does in fact begin to decrease at approximately the same value of dissolved sulphur dioxide that the observed decrease in the rate of dissolution of iron occurs.

CONCLUSIONS

1) It is suggested that the same mechanism is operative during the direct dissolution of both hydrated and anhydrous ferric oxide in acid media of pH less than one. This mechanism involves an ion exchange of surface hydroxyl groups for acid anions. The rate determining step is considered to be the desorption of a ferric-anion complex species from the oxide surface.

2) The dissolution of hydrated ferric oxide in acidified aqueous solutions of sulphur dioxide is thought to involve reaction of neutral sulphurous acid molecules at the oxide surface. It is suggested that this reaction may proceed in two different ways, depending on the concentration of dissolved sulphur dioxide, to produce either a cationic or a neutral ferric-sulphite complex on the oxide surface.

3) Depending on the conditions, it was observed that the rate of dissolution in aqueous sulphur dioxide solutions could be either heterogeneously or homogeneously controlled. It was found that, under conditions of homogeneous control, additions of cupric ion to the system could catalyse the rate until fully heterogeneous control was achieved. A mechanism has been postulated to explain these results.

4) It is thought that under conditions of heterogeneous control, the rate-determining step is the desorption of the ferric-sulphite complex from the oxide surface, and that reduction to ferrous iron takes place in the solution.

Application of Results

It has been shown that quite high rates of dissolution of hydrated ferric oxide in aqueous solutions of sulphur dioxide can be achieved at modest temperatures and pressures. For example, at 120°C the rate of dissolution in aqueous sulphur dioxide solution ($[SO_2]_{aq}$ = 0.139M) in the presence of perchloric acid and cupric ion ($[HClO_4]$ = 0.07M, $[Cu^{++}]$ = 0.003M) is approximately 25 times faster than in sulphuric acid solution of similar molar concentration. It is thought that iron oxide impurities in clay minerals may be leached rapidly with such solutions under mild pressure leaching conditions, especially as the surface area of a suspension of clay particles would be extremely large. Tests should be made on commercial clays to determine whether this process can offer an alternitive to the traditional dithionite leaching processes.

The application of the results of this study to the problem of the solution mining of deposits of iron oxide minerals is less clearly defined. Aqueous sulphur dioxide solutions should be cheap to produce, and this is a prime requisite for in situ leaching processes, since reagent loss is likely to be considerable. Provided that the ore-body could be sufficiently shattered, so that the surface area presented to the leach solution was large, and that the temperature within the ore-body could be maintained at above 100°C, then aqueous sulphur dioxide should be a suitable leaching agent. Iron oxide minerals containing copper impurities should be eminently suitable since these impurities would catalyse the rate of dissolution.

Suggestions For Future Work

This study has opened up several areas of work that could be usefully persued:

1) A comparison of the behavior of goethite and hematite under direct and reductive dissolution conditions. This should show whether in fact the oxide surfaces do take up similar configurations in aqueous solution and react similarly.

2) The present study should be extended to include higher concentrations of sulphur dioxide in solution. Also work at higher temperatures should prove interesting since goethite is reported to become unstable in aqueous solution in the temperature range 120-150°C. Quite marked increases in the rate of dissolution may occur under conditions where the goethite crystal structure is unstable.

3) A kinetic study of the homogeneous reactions of ferric ion with aqueous sulphur dioxide at elevated temperatures should be carried out. It should include a study of ferric-sulphur IV complexes, to determine which complexes, if any, are formed and under what conditions they occur. The reactions occurring in the heterogeneous systems cannot be fully understood until this type of information is available.

4) The feasibility of the anion exchange mechanism postulated to occur during the direct dissolution of iron oxide in acids could be investigated by measuring the rate of dissolution in acid solutions of sufficiently low pH for anion exchange to occur, and then observing the effect of increasing the anion concentration.

5) A study of the reactions of cupric ion with iron oxide under reducing conditions created by a hydrogen atmosphere may lead to a commercially feasible method of leaching iron oxides.

REFERENCES

1. Warren I.H., "Unit Processes in Hydrometallurgy", Vol. I, p. 300, Gordon and Breach (1964).

2. Warren I.H., Peters E., Byerley J., "Solution Mining", Reports submitted to Imperial Oil (Jan-April 1965).

3. Heeren, Pogg. Annalen, 7, 55 (1826).

4. Berthier, Ann. Chim., Phys. 7, 78 (1843).

5. Gelis, Bull. Soc., Chim., 5, 333 (1863).

6. Carpenter H.C.H., J. Chem. Soc., 81, 1 (1902).

7. Franck J., and Haber F., Ber. Berl. Akad., 250 (1931).

8. Albu H.W., and Schweinitz H.D. von, Ber. 65, 729 (1932).

9. Bassett H. and Henry A.J., J. Chem. Soc., 914 (1935).

10. Bassett H. and Parker W.G., J. Chem. Soc., 1540 (1951).

11. Higginson W.C.E. and Marshall J.W., J. Chem. Soc., 447 (1957).

12. Danilczuk E. and Swinarski A., Roczniki Chem., 35, 1563 (1961).

13. Karraker D.G., J. Phys. Chem., 67, 871 (1963).

14. Herring A.P. and Ravitz S.F., Trans. A.I.M.E., 232, 191 (1965).

15. Griffith R.H. and Morcom A.R., J. Chem. Soc., 786 (1945).

16. Mellor J.W., "Comp. Treat. on Inorg. and Theoret. Chem.", Vol XIII, p. 859ff., Longmans (1934).

17. Mayne J.E.O., J. Chem. Soc., 129 (1953).

18. Kulp J.L. and Trites A.F., Am. Mineralogist, 36, 23 (1951).

19. Weiser H.B., "Inorg. Colloid Chem.", Vol. II, p. 39, Wiley (1935).

20. Kataoka I., Mem. Fac. Agriculture, No. 5, Kochi Univ. (1959).

21. Glemser O., Ber. Dtsch. Chem., 70, 2117 (1937).

22. Glemser O. and Hartert E., Z. für Anorg. Chemie, 283, 111 (1956).

23. Gheith M.A., Am J. Sci., 250, 677 (1952).

24. Baudisch O. and Albrecht W.H., J. Am. Chem. Soc., 54, 943 (1932).

25. Van Schuylenborgh J. and Arens P.L., Recueil Trav. Chem., 69, 1557 (1950).

26. Welo L.A. and Baudisch O., Phil Mag. [7], 17, 753 (1934).

27. Veil S., Acad. des Sc. Compt. Rendus, 186, 753 (1928).

28. Bass A.M. and Benedict W.S., Astrophys. J., 116, 652 (1947).

29. Cabannes-Ott. C., Acad. des. Sc. Compt. Rendus, 224, 2491 (1957).

30. Cabannes-Ott C., Annales de Chemie, [13] 5, 954 (1960).

31. Duval C. and Lecomte J., Bull Soc. Chim. 8, 713 (1941).

32. Duval C. and Lecomte J., J. Chim Phys, 50, C64 (1953).

33. Hartert E. and Glemser O., Z. für Elektrochemie, 60, 746 (1956).

34. Glemser O. and Hartert E., Naturwissenschaften, 40, 552 (1953).

35. Frederickson L., Anal. Chem., 26, 1883 (1954).

36. Posnjak E. and Merwin H.E., Am. J. Sci., 47, 311 (1919).

37. Mackenzie R.C., "The D.T. Investigation of Clays", p. 299, Mineral. Soc. London (1957).

38. Kulp J.L. and Trites A.F., Am. Mineralogist, 36, 23 (1951).

39. Kelly W.C., Am. Mineralogist, 41, 353 (1956).

40. Belcher R., Gibbons D., and West T.S., Chem, and Indust., 73, 127 and 850 (1954).

41. Hunt W.G., Am. Water Works Assn. J., 45, 535 (1953).

42. Beazley W.B. et al, Dominion For. Ser. Bull. 93, Canada Dept. of Mines and Resources (1938).

43. Schmalz R.F., J. Geophys. Res., 64 No. 5, 575 (1959).

44. Smith F.G. and Kidd D.J., Am. Mineralogist, 34, 493 (1949).

45. Gruner J.W., Econ. Geol., 26, 442 (1931).

46. Azuma K. and Kametani H., Trans A.I.M.E., 230, 853 (1964).

47. Gayer K.H. and Wootner L., J. Phys. Chem., 60, 1569 (1956).

48. Schofield R.K., J. Soil Sci., $\underline{1}$, 1 (1949).

49. Ostwald W., J. prakt Chem., (2), $\underline{32}$, 314 (1885).

50. Barth K., Z. Phys. Chem., $\underline{9}$, 176 (1892).

51. Falk M. and Giguere D.A., Can J. Chem., $\underline{36}$, 1121 (1958).

52. Jones L.H. and McLaren E., J. Chem. Phys., $\underline{28}$, 995 (1958).

53. Cotton F.A. and Wilkinson G., "Advanced Inorganic Chemistry", p. 423, Interscience (1962).

54. Campbell W.B. and Maass O., Can. J. Res. 2, 42 (1930).

55. Campbell W.B. and Maass O., Pulp and Paper Mag., 599 (1930).

APPENDIX A

Tables of Experimental Results

Table I: Variation of rate with concentration of sulphuric acid (Figs. 2 and 3)

Temp = 130°C   1gm Goethite samples

$[H_2SO_4]$ (Mx10)	a_{H^+} (Mx10)	$d[Fe]/dt$ (Mx10^5/min)
1.46	1.46	0.25, 0.21
2.87	2.87	1.49, 1.34
4.08	4.08	2.32
5.47	5.47	3.18, 3.06
8.62	8.62	4.28, 4.10

Table II: Effect of temperature on rate of dissolution in sulphuric acid (Figs. 4 and 5)

$[H_2SO_4]$ = 0.146M   1gm Goethite samples

Temp °C	$\frac{10^3}{T°K}$	$d[Fe]/dt$ (Mx10^6/min)	$\log (\frac{d[Fe]}{dt})$
119	2.55	1.97	-4.706
128	2.49	2.46	-4.610
140	2.42	4.50	-4.347
147	2.38	6.84	-4.165

[HClO$_4$]		0.07 M		0.14 M		0.28 M	
Weight of sample		1 gm	2 gm	1 gm	2 gm	1 gm	2 gm
SO$_2$ p.p. (psig)	[SO$_2$]$_{aq}$ (Mx10)	$\frac{d(Fe)}{dt}$ (Mx10^5/min)					
5	0.83	----	----	0.327	0.324	0.280	-----
10	1.39	0.380 0.385 0.390	0.380	0.329 0.474	0.474 0.560	0.237 0.332 0.407	0.624
15	2.04	0.710	1.800	0.357 0.497	0.743	0.364 0.597	-----
18	2.30	-----	-----	0.510	0.624	-----	-----
20	2.63	0.655 0.610	-----	0.681	-----	0.465 0.485	-----
25	3.22	1.340	2.570	1.050	1.082 0.750	0.692	1.030
30	3.84	2.080	-----	1.720	-----	1.178	-----

Table III   Effect of varying dissolved sulphur dioxide concentration at different acidities
Temperature 110°C   (Figs. 9,10,11,17)

Table IV: Effect of acidity at constant dissolved sulphur dioxide
concentration

Temp = 110°C $[SO_2]_{aq}$ = 0.139M   1gm Goethite
                                                       samples

$[HClO_4]$ (Mx10)	$d[Fe]/dt$ (Mx10^8/min)
0.28	4.00
0.70	3.84
0.98	4.50
1.40	4.00
2.11	3.95
2.80	3.34
	Av. 3.94

Table V: Sulphate determinations

Temp. = 110°C   1gm Goethite samples
Determinations made after 3 hour run

$[HClO_4]$ (Mx10)	$[SO_2]_{aq}$ (Mx10)	$\frac{[SO_4^=]}{[Fe]}$
0.70	1.39	1.53
0.70	1.34	1.86
1.40	1.39	1.66
2.11	1.39	1.91
2.86	0.83	1.76
1.40	2.63	1.92
		Av. 1.77

Table VI: Effect of varying cupric ion concentration at constant acidity and constant sulphur dioxide concentration (Fig 12)

Temp = 110°C $[HClO_4]$ = 0.07M $[SO_2]_{aq}$ = 0.139M

$[Cu(ClO_4)_2]$ ($M \times 10^4$)	$d[Fe]/dt$ ($M \times 10^5$/min)	
	1gm sample	2gm sample
0	0.385	0.380
3.8	1.155	1.140
7.7	1.368	-----
15.3	1.820	3.620
30.6	2.250	4.550
61.0	4.600 5.320	9.270

Table VII: Effect of varying the concentration of dissolved sulphur dioxide at constant acidity and constant cupric ion concentration (Fig. 13)

Temp = 110°C $[HClO_4]$ = 0.07M $[Cu(ClO_4)_2]$ = 3.06×10^{-3}M   1gm Goethite samples

SO_2 p.p. (psig)	$[SO_2]_{aq}$ ($M \times 10^{-1}$)	$d[Fe]/dt$ ($M \times 10^5$/min)
10	1.39	2.250
15	2.04	2.400
20	2.63	3.820
25	3.22	3.550
30	3.84	2.320

Table VIII: Effect of dissolved sulphur dioxide concentration on copper in solution (Fig. 14)

Temp = 110°C $[HClO_4]$ = 0.07M   1gm Goethite sample

SO_2 p.p. (psig)	$[SO_2]_{aq}$ (Mx10)	[Cu] in soln. (Mx10^{-3})
0	0	3.06
10	1.39	2.51
25	3.22	2.51
30	3.84	2.31

Table IX: Effect of temperature on cupric catalysed reaction (Fig. 15)

$[HClO_4]$ = 0.07M $[SO_2]_{aq}$= 0.139M $[Cu(ClO_4)_2]$ = 3.06x10^{-3}M
1gm Goethite samples

Temp °C	$\frac{10^3}{T°K}$	d[Fe]/dt (Mx10^5/min)	$\log (\frac{d[Fe]}{dt})$
95	2.72	0.617	-5.210
100	2.68	1.275	-4.894
110	2.61	2.250	-4.648
120	2.545	4.420	-4.354

Table X: Typical heterogeneous rates in acidified aqueous sulphur dioxide
solutions

The following rates were measured under conditions of fully
heterogeneous control. They have been computed on the basis
of a specific surface area for the mineral of 90 cm^2/gm.
This value was calculated knowing the particle size range
(208-104μ) and the density of the mineral (approx. 4.2 gm/cc).
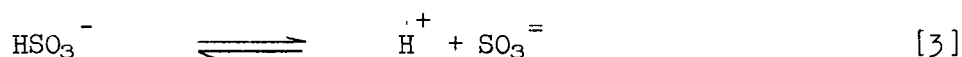The possible error in this calculation is thought to be $\pm$ 30%.

Temp = 110°C
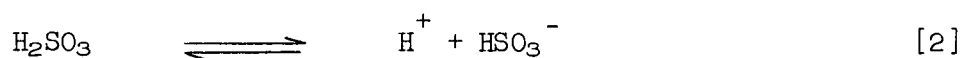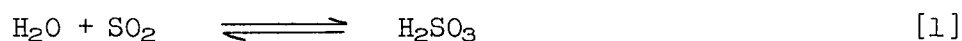
| $[SO_2]_{aq}$ (M)	$[HClO_4]$ (M)	$[Cu(ClO_4)_2]$ (Mx10^3)	d[Fe]/dt (Mx10^7/cm^2/min)
0.204	0.07	----	0.79
0.322	0.07	----	1.49
0.204	0.14	----	0.41
0.139	0.28	----	0.37
0.139	0.07	1.53	2.02
0.139	0.07	3.06	2.50
0.139	0.07	6.10	5.45

APPENDIX B

The Sulphur Dioxide-Water System

Solutions of sulphur dioxide in water have traditionally been referred to as solutions of sulphurous acid, H_2SO_3. The equilibria that were thought to be involved in such solutions were:

$$H_2O + SO_2 \rightleftharpoons H_2SO_3 \tag{1}$$

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \tag{2}$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^= \tag{3}$$

The second ionisation, reaction [3], was usually neglected since Ostwald[49] and Barth[50] showed that solutions of sulphurous acid act as if monobasic even to high dilutions.

Modern investigators[51,52] have attempted to identify H_2SO_3 in solution by infra-red absorption techniques but without success. It has been concluded that, in aqueous solutions of sulphur dioxide, undissociated sulphurous acid either does not exist or is present in only infinitesimal quantities. Undissociated dissolved sulphur dioxide is thought to exist in solution as a clathrate of the gas hydrate type[53]. The equilibria existing in aqueous solutions of sulphur dioxide are thought to be best represented as:

$$SO_2 + xH_2O \rightleftharpoons SO_2 \cdot xH_2O \tag{4}$$

$$SO_2 \cdot xH_2O \rightleftharpoons HSO_3^- + H_3O^+ + (x-2)H_2O \tag{5}$$
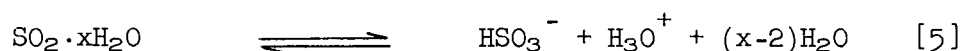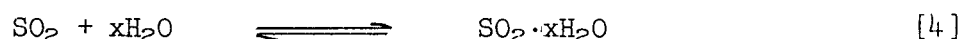
The apparent dissociation constant for "sulphurous acid" is given by:

$$K_a = \frac{[H^+][HSO_3^-]}{[SO_2]_{aq}^- [HSO_3^-]}$$ [6]

Campbell and Maass[54] calculated values of K_a from conductivity data obtained at various concentrations of dissolved sulphur dioxide and temperatures up to 90°C. They showed that K_a decreased with temperture, but was virtually independent of the concentration of dissolved sulphur dioxide up to 8%SO_2. These data are presented in Table BI. The solubility of sulphur dioxide in water at temperatures up to 120°C has been determined by Campbell and Maass[55]. The solubility data for the range of temperatures used in this study are presented in Table B II. A review of the literature including a compilation of reported data on the sulphur dioxide water system may be found in a publication by Beazley et al[42].

Knowing the total pressure in the system, the concentration of dissolved sulphur dioxide in solutions used in this study was determined directly from graphs plotted from the data in Table B II. The effects of variations in ionic strength on the solubility of sulphur dioxide were neglected.

The values of K_a at temperatures greater than 90°C were found by plotting log K_a versus $\frac{1}{T}$. This gave a straight-line relationship which could be extrapolated to higher temperatures. Knowing K_a, the concentration of bisulphite (HSO_3^-) could be calculated from equation [6], assuming that $[H^+]$ was equal to the concentration of perchloric acid in solution.

Table BI: Variation of K_a with temperature[54].

Temp °C	$K_a \times 10^3$
5	27.9
15	22.1
25	17.3
30	15.1
50	8.6
70	4.6
90	2.5

Table BII: Solubility of sulphur dioxide in water at various temperatures and various total pressures[55].

90°C		100°C		110°C		120°C	
cm.Hg	%$SO_2{}_{aq}$	cm.Hg	%$SO_2{}_{aq}$	cm.Hg	%$SO_2{}_{aq}$	cm.Hg	%$SO_2{}_{aq}$
97.1	1.05	127.5	1.03	166.3	1.01	213.0	1.00
144.5	2.02	182.5	1.97	230.0	1.93	284.5	1.89
186.6	3.00	230.8	2.93	283.0	2.87	344.0	2.82
231.8	3.81	280.1	3.72	338.0	3.63		
329.0	6.03						